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Evaluation of the Feasibility of Incinerating Hazardous Waste in High-Temperature Industrial Processes

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In the search for disposal alternatives, the U.S. Environmental Protection Agency is evaluating the potential use of high-temperature processes for the incineration of hazardous wastes. Many kinds of waste have already been disposed of in boilers and cement kilns; this report considers the many other potential processes, such as metallurgical furnaces, brick and lime kilns, glass furnaces, and sewage sludge combustors. Each process is examined against such criteria as time/temperature profile, geographical location, product quality considerations, institutional factors, and environmental impacts. Promising alternatives are identified.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Envrionmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes a methodology for evaluating the potential of high-temperature processes for destroying hazardous wastes. Many kinds of waste have already been disposed of in boilers and cement kilns; this report considers the many other potential processes such as metallurgical furnaces, brick and lime kilns, glass furnaces, and sewage sludge combustors. Each process is examined against such criteria as time/temperature profile, geographical location, product quality consideration, institutional factors, and environmental impacts. Further information on this subject may be obtained by contacting the Incineration Research Branch, Industrial Pollution Control Division, IERL-Ci.

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EVALUATION OF THE FEASIBILITY OF INCINERATING HAZARDOUS WASTE IN HIGH-TEMPERATURE INDUSTRIAL PROCESSES

by

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ABSTRACT

In the search for disposal alternatives, the U.S. Environmental Protection Agency is evaluating the potential use of high-temperature processes for the incineration of hazardous wastes. Many kinds of waste have already been destroyed in boilers and cement kilns; this report considers the many other potential processes, such as metallurgical furnaces, brick and lime kilns, glass furnaces, and sewage sludge combustors. Each process is examined against such criteria as time/temperature profile, geographical location, product quality considerations, institutional factors, and environmental impacts. Promising alternatives are identified.

The first task was to select common industries using high-temperature processes. Table 1 summarizes the screening criteria against which each process was evaluated.

TABLE 1. SCREENING CRITERIA FOR POTENTIAL HIGH-TEMPERATURE PROCESSES FOR THE DESTRUCTION OF HAZARDOUS WASTE

- Compatibility of process
  - Thermal destruction conditions: temperature and residence time (turbulence not considered)
  - Product quality
  - Potential for fugitive emissions
- Number of facilities
- Geographic matching of industry location and waste generators

The initial list of processes was based on operating temperature; any major process with an operating temperature of

greater than 650°C was included. The initial listing of approximately 100 processes included the metallurgical, chemical, and mineral industries and sludge and waste incinerators. When the other criteria in Table 1 were applied, several of these processes were eliminated from consideration

Table 2 lists those industries and processes that remained after several processes had been eliminated from further consideration by the application of the screening criteria. These processes were evaluated in more detail by use of a hazardous waste destruction model that compares temperature and residence times in the process with those required for complete (99.99%) destruction of various hazardous wastes.

Based on kinetic data on the constituents of the wastes, characteristic curves showing the various time-temperature combinations for destroying the wastes were obtained, as shown in Figure 1. For the industrial process, such information as the furnace volume, volumetric flow rate of gases, and temperature range of the furnace made it possible to plot "process curves" showing the residence time at which the furnace gas is above a certain temperature within the furnace. Laying the "process curves" over the hazardous waste characteristic curves made it possible to predict the waste categories destructible at various temperatures. Figure 2 shows this for a short rotary kiln. The required 99.99 percent destruction is predicted for those wastes whose lines are below and to the left of the process curves. Table 3 summarizes those processes evaluated in detail and the waste categories that are predicted to be 99.99 percent destroyable in each process.

Based on the process evaluation and discussions with many persons in industry and government, it is concluded that both technical and institutional factors are major obstacles to the use of high-temperature processes. The economics of each case have not been evaluated in detail,

TABLE 2. INDUSTRIES AND PROCESSES SELECTED FOR FURTHER HAZARDOUS WASTE DESTRUCTION EVALUATION

Industry	Process or furnace	Exit and maximum temperature, °C	Residence time (seconds, unless otherwise noted)[a]
Brick	Tunnel kiln	260-1180	4.3
Carbon black	Oil furnace process	870-1400	1.1
Primary copper	Reverberatory furnace	1300-1400	2.2
Primary lead	Blast furnace	700-1200	5.9
Primary zinc	Multiple-hearth roaster	200-980	>10
	Suspension roaster	930-1010	>10
	Fluidized-bed roaster	950-1740	>10
Iron and steel	Blast furnace	1100[b]-1870	1.1[c]
	Open-hearth furnace	1200-1800	2.0
Lime	Long rotary kiln	680-1900	8.3
	Short rotary kiln with stone preheater	1160-1840	7.6
Lightweight aggregate	Rotary kiln	370-1150	3.6
Glass	Melting furnace	620-1480	4.1
Sewage sludge	Fluid-bed furnace	760-870	1.4
	Multiple-hearth furnace	480-980	0.5
Hazardous waste incineration[d]	Rotary kiln	820-1600	2.0 s to 2 h[e]
	Liquid injection	700-1650	0.5 to 2

[a] Residence time above the greater of the exit temperature or 760°C.

[b] Represents estimated temperature at the top of the combustion zone in the blast furnace.

[c] Residence time has been calculated using 33% of the total furnace volume.

[d] Included for comparison only.

[e] The residence time for solids and sludges can be adjusted.

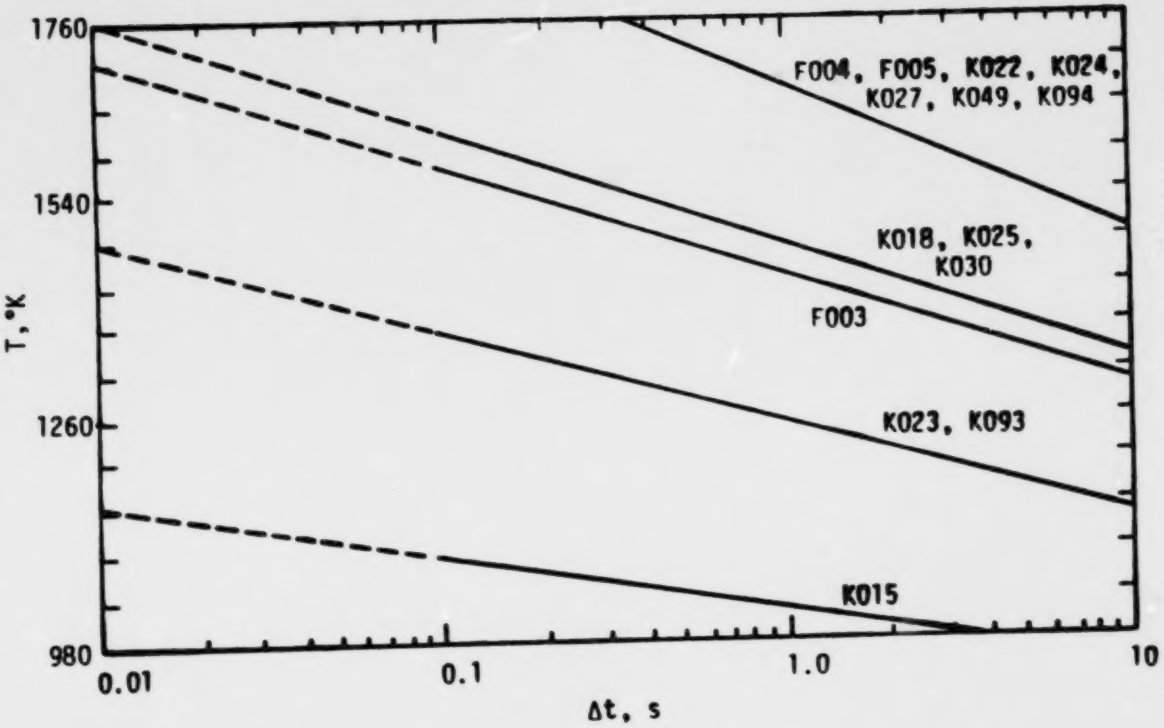

Figure 1. Plots of time-temperature requirements for 99.99 percent destruction of selected hazardous waste categories.

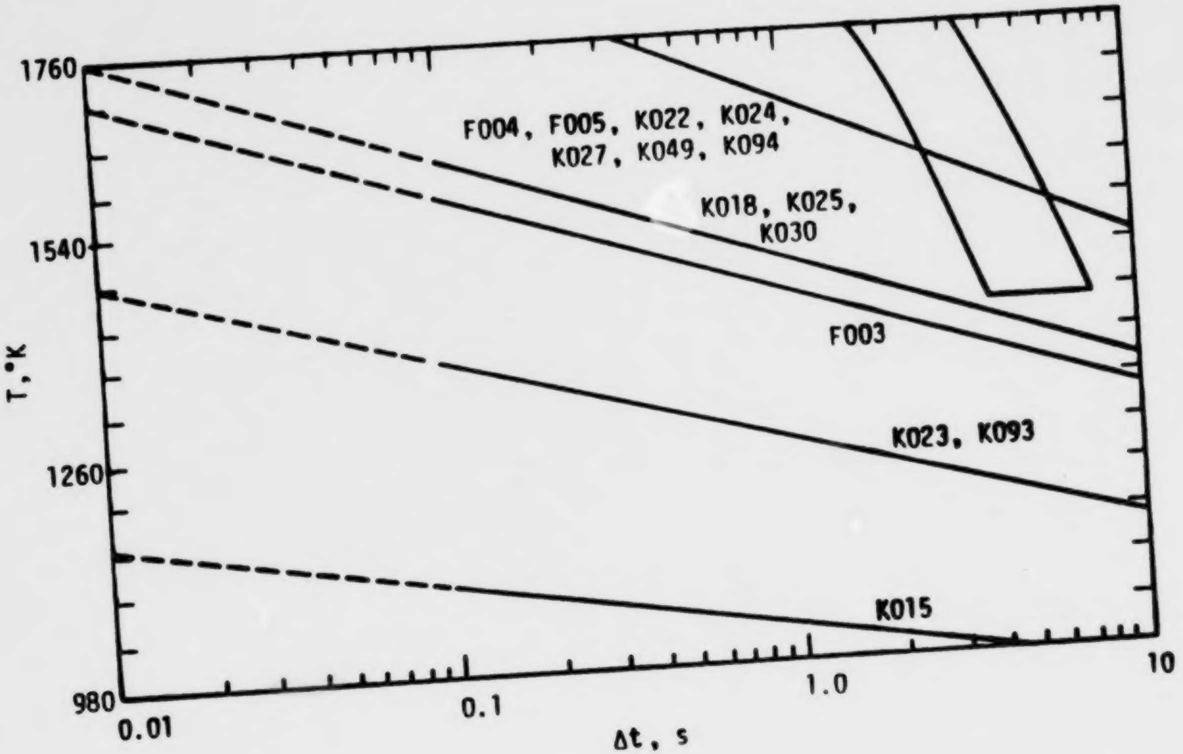

Figure 2. Hazardous waste destructibility for the short rotary lime kiln.

TABLE 3. HAZARDOUS WASTE CATEGORIES THAT ARE PREDICTED DESTRUCTIBLE (99.99%) IN SELECTED INDUSTRIAL PROCESSES

Industry	Process or furnace	Waste category						
		K015	K023, K093	F003	K018 K030	K025	F004, F005	K022, K024, K027 K049, K094
Brick	Tunnel kiln	Yes	Yes	No	No	No	No	No
Carbon black	Oil furnace process	Yes	Yes	Maybe	No	No	No	No
Glass	Melting furnace	Yes	Yes	Yes	Yes	Yes	No	No
Iron and steel	Blast furnace	No	Yes	Yes	No	No	Yes	No
	Open-hearth furnace	No	Yes	Yes	No	Yes	Yes	No
Lightweight aggregate	Rotary kiln	Yes	Yes	No	No	No	No	No
Lime	Long and short rotary kilns	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Primary copper	Reverberatory furnace	No	Yes	Yes	No	Yes	No	No
Primary lead	Blast furnace	Yes	Yes	No	No	No	No	No
Primary zinc	Multiple-hearth roaster	Yes	No	No	No	No	No	No
	Suspension roaster	Yes	Yes	No	No	No	No	No
	Fluid-bed roaster	Yes	Yes	No	No	No	No	No
Sewage sludge	Fluid-bed furnace	Yes	No	No	No	No	No	No
	Multiple-hearth furance	Yes	No	No	No	No	No	No

but they will clearly be proportional to energy cost factors and the degree of hazard associated with the waste. The driving force to utilize high-temperature processes must come from the companies involved. The availability of low- or zero-cost energy combined with possible disposal fees from the generators must be sufficiently attractive to justify the effort required to conduct test burns and make the necessary process modifications.

SECTION 1

INTRODUCTION

Approximately 36 billion kilograms (40 million short tons) of hazardous waste is generated annually in the United States by some 270,000 industrial plants and other facilities. Most of this waste is now landfilled, but alternative waste disposal methods are under consideration that allow for the recovery of heat (through incineration) or valuable constituents (through recycling). The rising costs of transportation and landfilling and the increasingly stringent RCRA regulations governing land disposal of organic liquids will undoubtedly lead to more interest in thermally destroying hazardous waste or reducing their quantity through recycling.

High-temperature industrial processes are being considered as an alternative means of thermal destruction. The Incineration Research Branch of the U.S. Environmental Protection Agency (EPA) is involved in the investigation, evaluation, and development of thermal destruction techniques for the disposal of hazardous waste. Two high-temperature processes (industrial boilers and cement kilns) are already being evaluated as possible thermal destruction candidates, and many kinds of wastes have already been destroyed in these processes. The Agency's interest in other possible high-temperature industrial processes for this purpose prompted the initiation of this feasibility screening study.

The objectives of this study were to locate processes that offer suitable combustion conditions, to provide uniform criteria for the selection of processes that appear to have the greatest potential for waste destruction, and to examine the selected processes for overall consideration.

In the selection of possible processes, the first task was to find common industries using high-temperature processes. Typical operating parameters of various processes were obtained from the literature, trade associations, and industry contacts. Any process with an operating temperature greater than 650°C (1200°F) was included. This temperature is believed to be the minimum temperature allowable for the destruction of the wastes under consideration. The initial listing contained approximately 100 processes from the metallurgical, chemical, and mineral industries, and sludge and waste incinerators.

The processes on this list were then evaluated against the following screening criteria for their potential use in the destruction of hazardous wastes:

- Compatibility of process
    - Thermal destruction conditions (temperature and residence time; turbulence not considered)
- Number of facilities
- Geographic matching of industrial location and waste generators.

As a result of this screening effort, the list was narrowed down to processes in the following industries, each of which is addressed in this report:

Brick and tile
Carbon black
Glass
Iron and steel
Light-weight aggregate
Lime
Primary copper
Primary lead
Primary zinc
Sewage sludge incinerators

Section 2 of the report discusses the characteristics and sources of hazardous wastes considered for thermal destruction.

Section 3 presents the hazardous waste destruction model developed to identify those processes most applicable for the destruction of hazardous wastes. Section 4, which composes the major part of the report, presents an assessment of each of the high-temperature industrial processes selected as the most promising candidates for hazardous waste destruction. Appendices A and B present backup data for the selection process.

SECTION 2

WASTE SELECTION AND CHARACTERIZATION

2.1 SELECTION AND WASTE COMPONENT CHARACTERIZATION

In this assessment, the selection of specific hazardous wastes as candidates for thermal destruction in an industrial process is of primary importance in examining this method as a means of destroying these wastes. The type of waste selected and its characteristics play a major role in determining the process operating conditions (temperature and residence time) required for complete destruction. This information also aids in assessing the impact on the process hardware and the emission control system and ultimately determines the compatibility of the wastes with a proposed process in an industrial facility.

Initially, all hazardous waste categories from specific and nonspecific sources (as found in Parts 261.31 and 261.32, 46 FR 27476) were considered potential candidates for thermal destruction. Certain waste categories, however, were eliminated during preliminary review because of their low combustibility or their explosive nature. The waste types produced by the following industries were eliminated from consideration: inorganic pigments, inorganic chemicals, explosives, iron and steel, and secondary lead. Most of these industries generate waste streams that are highly inorganic in nature and hence not suitable for combustion.

After the preliminary review, more detailed information gathered and compiled on the remaining waste categories led to the elimination of additional wastes because of the low combustibility of their components. Appendix B presents background data (physical state, composition, present disposal practices, geographic distribution, and annual generation rate) for those waste categories included in this initial screening. Background information collected on all waste categories was obtained from EPA's Resource Conservation and Recovery Act, Subtitle C, Identification and Listing of Hazardous Waste, Background Document.[1]

The hazardous waste categories that were ultimately selected for further evaluation were those in which the wastes appeared to exhibit high combustibility or incinerability. The definition of incinerability here is considered to be the relative ease with which flame incineration can completely oxidize a constituent to its final products of combustion.[2] The ease of incinerability can be related to the heat of combustion of each constituent.[2] The heat of combustion was estimated for each waste category by use of the heat of combustion for each of the principal organic hazardous constituents. These data were then used to predict incinerability. This predicted incinerability was, in turn, used as a basis for the selection of potential hazardous waste candidates for thermal destruction in high-temperature industrial processes.

Table 2-1 presents the selected waste candidates, the type of generating industry and its SIC code, and a description of the waste. The Organic Chemicals Industry generates most of the wastes selected for consideration.

Table 2-2 presents a characterization of the hazardous waste types and their components. Most wastes are composed of several constituents. In general, wastes from nonspecific sources (those in the F series) vary considerably in composition among the different processes, whereas wastes from specific sources (those in the K series) tend to be more consistent in the type and percentage of each waste component.

2.2 MATHEMATICAL MODEL FOR RATE OF THERMAL DESTRUCTION OF HAZARDOUS WASTES

2.2.1 Theory

The chemical reaction sequence involved in the destruction of organic constituents present in hazardous wastes is a

TABLE 2-1. DESCRIPTION OF SELECTED HAZARDOUS WASTE STREAMS

Hazardous waste No.	Waste generating industry		Description of waste
	Type	SIC	
F003	Nonspecific sources		Spent nonhalogenated solvents and still bottoms from the recovery of these solvents
F004	Nonspecific sources		Spent nonhalogenated solvents and still bottoms from the recovery of these solvents
F005	Nonspecific sources		Spent nonhalogenated solvents and still bottoms from the recovery of these solvents
K015	Organic chemicals	2865	Still bottoms from the distillation of benzyl chloride
K018	Organic chemicals	2869	Heavy ends from the fractionation column in ethyl chloride production
K022	Organic chemicals	2869	Distillation bottom tars from the production of phenol/acetone from cumene
K023	Organic chemicals	2869	Distillation light ends from the production of phthalic anhydride from naphthalene
K024	Organic chemicals	2869	Distillation bottoms from the production of phthalic anhydride from naphthalene
K025	Organic chemicals	2865	Distillation bottoms from the production of nitrobenzene by the nitration of benzene
K027	Organic chemicals	2869	Centrifuge and distillation residues from toluene diisocyanate production
K030	Organic chemicals	2869	Column bottoms or heavy ends from the combined production of trichloroethylene and perchloroethylene
K049	Petroleum refining	2911	Slop oil emulsion solids from the petroleum refining industry
K093	Organic chemicals	2869	Distillation light ends from the production of phthalic anhydride from ortho-xylene
K094	Organic chemicals	2869	Distillation bottoms from the production of phthalic anhydride from ortho-xylene

TABLE 2-2. PHYSICAL DATA FOR ORGANIC CONSTITUENTS OF HAZARDOUS WASTE CATEGORIES AND WASTE GENERATION RATES

Hazardous waste number (physical state)	Chemical compound[a] (% of total)	Melting point,[b] °C	Boiling point,[b] °C	Specific gravity[b]	Heat of combustion,[c] kcal/g	Annual generation rate,[a,d] Mg
F003 (organic liquid and sludges)	o-Xylene	-25.0	144	0.880		489,900[e]
	m-Xylene	-48.0	139	0.860		(all xylenes)
	p-Xylene	13.0	138	0.861		
	Ethylbenzene	-95.0	136	0.867		54,430[e]
	Cyclohexanone	-45.0	155	0.947		9,072[e]
	Acetone	-95.4	56.2	0.792	7.36	86,200[e]
	Ethylacetate	-83.6	77	0.894	6.12	69,900[e]
	Ethylether	-116	34.5	0.715		54,430[e]
	Methyl isobutyl ketone	-85.0	116	0.804		78,000[e]
	n-Butyl alcohol	-89.0	118	0.811	8.62	45,360[e]
	Methanol	-97.8	64.5	0.792	5.70	317,500[e]
F004 (organic liquid and sludges)	O-Cresol	31.0	191	1.03	8.18	11,800[e]
	m-Cresol	11.0	201	1.03	8.18	(cresols and cresylic acid)
	p-Cresol	35.0	220-250	1.02-1.07	8.09	
	Cresylic acid	20-76	220-250	1.02-1.07	8.09	
	Nitrobenzene	5.7	211	1.20	6.01	9,072[e]
F005 (organic liquid and sludges)	Toluene	-94.5	111	0.866	10.14	317,500[e]
	Pyridine	-42	115	0.982	7.83	907[e]
	Methylethyl ketone	-85.9	79.6	0.805	8.07	
	Carbon disulfide	-109	46.3	1.26		77,100[e]
	Isobutanol	-108	107	0.806		18,600[e]
K015 (organic sludge)	Benzylchloride	-39	179	1.10	6.18	5,300
	Trichlorobenzene	17-63.5	209-219	1.57	3.40	
	Tetrachlorobenzene	47-138	246-254	1.73	2.61	
	Pentachlorobenzene	86	277	1.83	2.05	
	Hexachlorobenzene	228	326	2.04	1.79	
	Benzotrichloride	-5	220	1.38	3.90	
	Chlorobenzene	-45.2	131	1.11	6.60	
	Toluene	-94.5	111	0.866	10.14	
K018 (organic liquid)	Ethylchloride (3%)	-139	13.0	0.917	3.00	35,000
	1,2-dirchloroethane (22%)	-35.3	83.7	1.26	3.00	
	Hexachlorobenzene	228	326	2.04	1.79	
	1,1,1-Trichloroethane	-38	75	1.32	1.99	
	Hexachlorobutadiene	-22	210-220	1.68	2.12	
	Trichloroethylene (32%)	-73	86.7	1.46	1.74	
K022 (organic sludge)	Acetone	-94.3	56.2	0.792	7.36	45,000-100,000
	Phenol	42.5	182	1.07	7.78	
	Cumene	-96	152	0.862		
	PAH[f] (90%)					
K023 (organic liquid)	Phthalic anhydride (90)	131	285	1.53	5.29	950
	Maleic anhydride (10%)	53	200	0.934	3.40	
K024 (organic sludge)	Phthalic anhydride (50%)	131	285	1.53	5.29	2,300
	1,4-Naphthoquinone (50%)	123-126	Sublimes		6.97	

(continued)

TABLE 2-2 (continued)

Hazardous waste number (physical state)	Chemical compound[a] (% of total)	Melting point,[b] °C	Boiling point,[b] °C	Specific gravity[b]	Heat of combustion,[c] kcal/g	Annual generation rate,[a,d] Mg
K025 (organic sludge)	m-Dinitrobenzene (94%)	89.9	303	1.55	4.15	170-200
	2,4 Dinitrotoluene (6%)	70.5	300	1.32	4.68	
	Nitrobenzene (trace)	5.7	211	1.20	6.01	
K027[g] (organic sludge)	Toluene diisocyanate (<3%)	19-22	251	1.22	5.92	6,000
	Toluene diamines (<3%)	99	280		8.24	
	Polymers and tarlike materials (90%)				5-9	
K030 (organic liquid)	1,1,2,2-Tetrachloroethane (23%)	-44	146	1.60	1.39	15,000
	Hexachlorobutadiene (34%)	-22	210-220	1.68	2.12	
	Hexachlorobenzene (20%)	228	326	2.04	1.79	
	1,1,1,2-Tetrachloroethane (6%)	68	130	1.55	1.39	
	Ethylene dichloride (4%)	-36	84	1.25	1.90	
	Hexachloroethane	186	186	2.09	0.46	
	Pentachloroethane (3%)	-29	162	1.68	0.53	
	Perchloroethylene (4%)	-22	121	1.63	1.19	
	1,1,2-Trichloroethane (4%)	-36.4	114	1.44	1.99	
K049[h] (sludge)	H_2O (40%)	0	100	1.00		2,000-10,000
	Oil (34-43%)			0.83-0.87	10-11	
	Phenol (14 ppm)	42.5	182	1.07	7.78	
	Sand, silt (12%)					
K093	Phthalic anhydride (>90%)	131	285	1.53	5.29	2,300
	Maleic anhydride (trace)	53	200	0.934	3.40	
K094 (organic sludge)	Phthalic anhydride (>90%)	131	285	1.53	5.29	410

[a] Ref. 1.

[b] Ref. 5.

[c] Ref. 2.

[d] Data is based on generation rate in 1979 and 1980.

[e] Quantities for F003, F004, and F005 are based on solvent usage and may be larger if including other applications. The generation rate is amount generated which is not an exact indication of the amount to be incinerated since some of these solvents are recovered and reused. Depending on the recovery process the still bottoms contain 5-50% of the original solvent. Most U.S. recovery processes result in an average of 25% solvent in still bottoms.

[f] Polycyclic aromatic hydrocarbons.

[g] Highly reactive. Also contains 6% ferric chloride.

[h] Also contains diatomaceous earth and trace metal contaminants, especially chromium and lead.

complicated process consisting of a series of decomposition, polymerization, and free radical reactions. The destructive processes of significance in incineration are pyrolysis (thermolytic cracking) and oxidation.[3] In general, at sufficiently high temperatures, the overall reaction rate can be conservatively described by first order kinetics.[4]

Because the processes under consideration are all above 760°C (1400°F), the hazardous wastes included in the study should go from a liquid phase to a gas phase soon after they enter the high-temperature processes. Based on the assumption that the hazardous waste is in the gas phase before any decomposition or oxidation occurs, the rate of disappearance of any organic hazardous waste constituent can be described by first order kinetics as:

$$\frac{dC_A}{dt} = -kC_A \qquad (1)$$

where C_A = the concentration of hazardous constituent A at time t

k = the reaction rate constant

The solution to Equation 1 can be expressed as:

$$\ln \frac{C_A}{C_{AO}} = -k\,\Delta t \qquad (2)$$

where C_{AO} = initial concentration of hazardous constituent A

Δt = time required to reach final concentration C_A

The temperature dependence of the reaction rate constant k can be correlated by the Arrhenius equation:

$$k = A \exp(-E/RT) \qquad (3)$$

where A = Arrhenius pre-exponent frequency factor (S^{-1})
E = Energy of activation (J/kg-mole)
R = Universal gas constant (8314 J/kg-mole-°K)
T = Absolute temperature (°K)

For 99.99 percent destruction of a hazardous waste constituent, the left-hand concentration term in Equation 2 is:

$$\ln \frac{C_A}{C_{AO}} = -9.21 \qquad (4)$$

Substituting Equation 4 for $\ln \frac{C_A}{C_{AO}}$ and Equation 3 for k in Equation 2, the time Δt required for 99.99 percent destruction of a compound can be represented as:

$$\ln \Delta t = \ln \left(\frac{9.21}{A}\right) + \frac{E}{RT} \qquad (5)$$

2.2.2 Time-Temperature Curves for Destruction of Selected Waste Categories

A literature search was conducted to obtain kinetic data (A and E values) for organic compounds associated with the selected hazardous waste categories. Table 2-3 presents the results. As the data column indicates, kinetic data were not available for many of the organic constituents in the wastes. Most of the available data were on pyrolytic destruction as opposed to oxidative destruction. The pyrolysis data represent either decomposition into stable molecules or production of free radicals by cleavage of a specific bond in the compound. In some cases where pyrolysis data were not available for a specific compound, values of A and E are presented for the limiting compound in the destruction of the particular complex (Table 2-4 indicates the limiting compound in the destruction of several organic complexes).

Several assumptions were involved in the choice of appropriate A and E values for the hazardous waste categories from the kinetic data for the organic waste constituents. A conservative approach was taken by representing the hazardous waste by A and E values corresponding to the worst-case compound (most difficult to destroy) in that category. Pyrolysis data instead of oxidation data were used whenever they were available because they are the most conservative.[3] Table 2-5 presents the relative

TABLE 2-3. KINETIC DATA FOR COMPOUNDS PRESENT IN CANDIDATE HAZARDOUS WASTES

Hazardous waste No.	Chemical compound	Kinetic parameters			Type of data[a]
		A (s^{-1})	E MJ/kg-mole	(Btu/lb mole)	
F003	o-xylene	4.8×10^{12}	314	(1.35×10^{5})	P
	m-xylene	4.2×10^{12}	325	(1.40×10^{5})	P
	p-xylene	4.8×10^{12}	318	(1.37×10^{5})	P
	Ethyl benzene	1.0×10^{13}	263	(1.13×10^{5})	P
	Cyclohexanone	-[b]	-	-[b]	
	Acetone	-	-	-	
	Ethyl acetate	3.2×10^{12}	200	(8.60×10^{4})	P
	Ethyl ether	-	-	-	
	Methyl isobutyl ketone	-	-	-	
	n-butyl alcohol	4.8×10^{14}	277	(1.19×10^{5})	P
F004	Cresols	-	-	-	
	Cresylic acid	-	-	-	
	Nitrobenzene	2.1×10^{12}	325	(1.40×10^{5})	P
F005	Toluene	2.1×10^{12}	325	(1.40×10^{5})	P
	Methyl ethyl ketone	-	-	-	
	Pyridine	-	-	-	
	Carbon disulfide	-	-	-	
	Isobutanol	4.8×10^{14}	277	(1.19×10^{5})	P
K015	Benzyl chloride	-	-	-	
	Trichlorobenzene	-	-	-	
	Tetrachlorobenzene	-	-	-	
	Pentachlorobenzene	-	-	-	
	Hexachlorobenzene	1.9×10^{16}	304	(1.31×10^{5})	O
	Chlorobenzene	-	-	-	
K018	Ethyl chloride	4.0×10^{14}	284	(1.22×10^{5})	P
	1,2-dichloroethane	1.0×10^{13}	293	(1.26×10^{5})	P
	Hexachlorobenzene	1.9×10^{16}	304	(1.31×10^{5})	O
	1,1,1-trichloroethane	3.2×10^{12}	200	(8.62×10^{4})	P
	Hexachlorobutadiene	2.1×10^{12}	325	(1.40×10^{5})	P
	Trichloroethylene	-	-	-	

(continued)

TABLE 2-3 (continued)

Hazardous waste No.	Chemical compound	Kinetic parameters			Type of data[a]
		A (s^{-1})	E MJ/kg-mole	(Btu/lb mole)	
K022	Acetone	-	-	-	
	Phenol	-	-	-	
	Cumene	3.2×10^{13}	242	(1.04×10^5)	P
	Tars	-	-	-	
K023	Phthalic anhydride	-	-	-	
	Maleic anhydride	1.0×10^{13}	293	(1.26×10^5)	P
K024	Phthalic anhydride	-	-	-	
	1,4-naphthaquinone	-	-	-	
K025	m-dinitrobenzene	-	-	-	
	2,4-dinitrotoluene	-	-	-	
	Nitrobenzene	2.1×10^{12}	325	(1.40×10^5)	P
K027	Toluene diisocyanate	-	-	-	
	Toluene diamines	-	-	-	
	Polymer tarlike material	-	-	-	
K030	1,1,2,2-tetrachloroethane	1.0×10^{13}	293	(1.26×10^5)	P
	Hexachlorobutadiene	2.1×10^{12}	325	(1.40×10^5)	P
	Hexachlorobenzene	1.9×10^{16}	304	(1.31×10^5)	O
	1,1,2,2-tetrachloroethane	-	-	-	
	Ethyl chloride	4.0×10^{14}	253	(1.09×10^5)	P
	Trichloroethylene	-	-	-	
	1,1,2-trichloroethane	3.2×10^{12}	200	(8.62×10^4)	P
	Pentachloroethane	1.0×10^{13}	293	(1.26×10^5)	P
K049	Phenol	-	-	-	
	Oil	-	-	-	
K093	Phthalic anhydride	-	-	-	
	Maleic anhydride	1.0×10^{13}	293	(1.26×10^5)	P
K094	Phthalic anhydride	-	-	-	

[a] P - Pyrolysis.
O - Oxidation.

[b] Blanks indicate no data were available.

TABLE 2-4. WORST CASE COMPOUND FOR DESTRUCTION BY STRUCTURAL CLASS[4]

Compound	Limiting compound	Reasoning[a]
Methyl chloride	Methane	UCT
Methylene chloride	Methane	UCT
Chloroform	Methane	Analogy
Carbon tetrachloride	Methane	Analogy
Carbon disulfude	Dichloroproprane	UCT
Trichloroethanes	Propane	UCT
Tetrachloroethanes	Propane	Analogy
Pentachloroethanes	Propane	Analogy
Hexachloroethanes	Propane	Analogy
Trichlorotrifluoroethane	Propane	Analogy
Vinylidene chloride	Vinyl chloride	UCT
Trichloroethylene	Propane	UCT
Perchloroethylene	Propane	Analogy
Bis(chloromethyl)ether	Dichloroethane	Analogy with bis(2-chloromethyl) ether
Chloropropane	Propane	TP
Dichloropropane	Propane	UCT
Trichloropropane	Dichloroethanes	UCT
Dichloropropanols	Propane	Analogy
Epichlorohydrin	Dichloroethane	UCT
Isobutanol	Propane	UCT
Chlorobutadiene	Toluene	Analogy
Hexachlorobutadiene	Toluene	UCT
Maleic anhydride	Dichloroethane	UCT
Bis(2-chloroethyl)ether	Dichloroethane	UCT
Methyl ethyl ketone	Dichloroethane	UCT
Methyl isobutyl ketone	Dichloroethane	UCT
Chlorobenzene	Hexachlorobenzene	UCT
Dichlorobenzene	Hexachlorobenzene	UCT
Trichlorobenzene	Hexachlorobenzene	UCT
Tetrachlorobenzene	Hexachlorobenzene	Analogy
Pentachlorobenzene	Hexachlorobenzene	Analogy
Pyridine	Methane	UCT

(continued)

TABLE 2-4 (continued)

Compound	Limiting compound	Reasoning[a]
Nitrobenzene	Toluene	UCT
Phenol	Methane	UCT
Chlorophenol	Methane	Analogy
Dichlorophenol	Methane	Analogy
Trichlorophenol	Methane	Analogy
Tetrachlorophenol	Methane	Analogy
Pentachlorophenol	Methane	Analogy
Nitrophenols	Methane	Analogy
Benzotrichloride	Dichloroethane	UCT
Cresols	Benzene	UCT
Cresylic acid	Benzene	Analogy
Nitrocresols	Benzene	Analogy
Dinitrocresols	Benzene	Analogy
Aceteophenone	Toluene	UCT
Phthalic anhydride	Propane	UCT
Dimethyl phenols	Methane	Analogy
Cumyl phenol	Methane	Analogy
Naphthalene	Propane	UCT
Naphthoquinone	Propane	Analogy

[a] UCT - Union Carbide predicted temperature.
TP - Thermal pyrolysis data.
Analogy - Structural correlation and speculation.

TABLE 2-5. ORDER OF INCREASING DESTRUCTIBILITY BASED ON TEMPERATURE REQUIRED FOR 99.99 PERCENT DESTRUCTION AT 1-SECOND RESIDENCE TIME[3]

Order	Compound	Temperature[a] °C	(°F)
1	Methyl chloride	844	(1550)
2	Methane	836	(1535)
3	Phenol	807	(1484)
4	Methylene chloride	797	(1466)
5	Pyridine	791	(1455)
6	Chlorobenzene	768	(1413)
7	Dichlorobenzene	765	(1408)
8	Hexachlorobenzene	763	(1405)
9	Ethane	761	(1401)
10	Vinyl chloride	746	(1374)
11	Ethyl chloride	737	(1358)
12	Benzene	737	(1358)
13	Cresol	722	(1331)
14	Ethylene	721	(1329)
15	Toluene	720	(1327)
16	Nitrobenzene	720	(1327)
17	Hexachlorobutadiene	719	(1325)
18	Trichlorobenzene	716	(1320)
19	Vinylidene chloride	712	(1313)
20	Acetophenol	711	(1310)
21	Propane	708	(1305)
22	1,2,2-trichloro-1,1,2-trifluoroethane	692	(1277)
23	Dichloropropane	686	(1266)
24	Trichloroethane	683	(1260)
25	Phthalic anhydride	672	(1240)
26	Isobutanol	666	(1229)
27	Trichloroethylene	662	(1222)
28	Naphthalene	661	(1221)
29	Methyl ethyl ketone	657	(1213)
30	Dichloroethane	656	(1212)
31	Epichlorohydrin	618	(1143)
32	Maleic anhydride	607	(1123)
33	Bis(2-chloroethyl) ether	602	(1115)
34	Methyl isobutyl ketone	599	(1109)
35	Trichloropropane	571	(1060)
36	Benzotrichloride	528	(982)
37	Carbon disulfide	400	(751)

[a] Temperature required for 99.99 percent destruction at a residence time of 1 second.

destructibilities of various organic compounds based on their autoignition temperatures. This listing was used to determine the worst-case compound for several hazardous waste categories. If the compounds did not appear on this table, heat of combustion was used to determine the worst-case compound, i.e., the lower the heat of combustion, the more difficult the combustion of the compound is believed to be.

In cases where kinetic data were not available for a compound, an arbitrary conservative A value of 1.0×10^{10} s^{-1} and E value of 293 MJ/kg-mole (1.26×10^5 Btu/lb-mole) were assigned.[3] It should be noted that low A values ($<1.0 \times 10^{10}$) and high E values ($>1.26 \times 10^5$) do not usually occur with the same compound.

Table 2-6 presents the composite kinetic parameters for the hazardous waste categories. Based on the relationship derived for estimating time-temperature requirements for 99.99 percent destruction (Equation 5, Section 2.2.1), plots of time-temperature relationships were constructed for the selected hazardous waste categories. Figure 2-1 depicts the predicted linear gas phase time-temperature plots. Because the kinetic behavior of the waste categories is uncertain at times less than 0.1 second, dotted lines are used to extend the time-temperature relationships below 0.1 second.

2.3 SUMMARY OF WASTE CHARACTERISTICS

Table 2-7 summarizes the reported characteristics of each selected waste. The approximate waste heating values were obtained from the literature.[2,6] When specific data were not available, estimates were based on an approximate waste density and an assumed average waste heating value of 33.5 MJ/liter (120,000 Btu/gal).[3] The kinetic data were obtained from tables in the preceding subsection, and the remaining data were taken from Table 2-2.

TABLE 2-6. COMPOSITE KINETIC PARAMETERS FOR HAZARDOUS WASTE CATEGORIES

Hazardous waste No.	Worst case compound	Kinetic parameters	
		A, s^{-1}	E, MJ/kg-mol (Btu/lb-mol)
F003	Xylene	4.2×10^{12}	325 (1.40×10^5)
F004	Cresols	1.0×10^{10}[a]	293 (1.26×10^5[a])
F005	Pyridine	1.0×10^{10}[a]	293 (1.26×10^5[a])
K015	Hexachlorobenzene	1.9×10^{16}	304 (1.31×10^5)
K018	Hexachlorobutadiene	2.1×10^{12}	325 (1.40×10^5)
K022	Phenol	1.0×10^{10}[a]	293 (1.26×10^5[a])
K023	Maleic anhydride	1.0×10^{13}	293 (1.26×10^5)
K024	Phthalic anhydride	1.0×10^{10}[a]	293 (1.26×10^5[a])
K025	Nitrobenzene	2.1×10^{12}	325 (1.40×10^5)
K027	Toluene diisocyanate	1.0×10^{10}[a]	293 (1.26×10^5[a])
K030	Hexachlorobutadiene	2.1×10^{12}	325 (1.40×10^5)
K049	Phenol	1.0×10^{10}[a]	293 (1.26×10^5[a])
K093	Maleic anhydride	1.0×10^{13}	293 (1.26×10^5)
K094	Phthalic anhydride	1.0×10^{10}[a]	293 (1.26×10^5[a])

[a] Conservative values were assigned where kinetic data were not available.

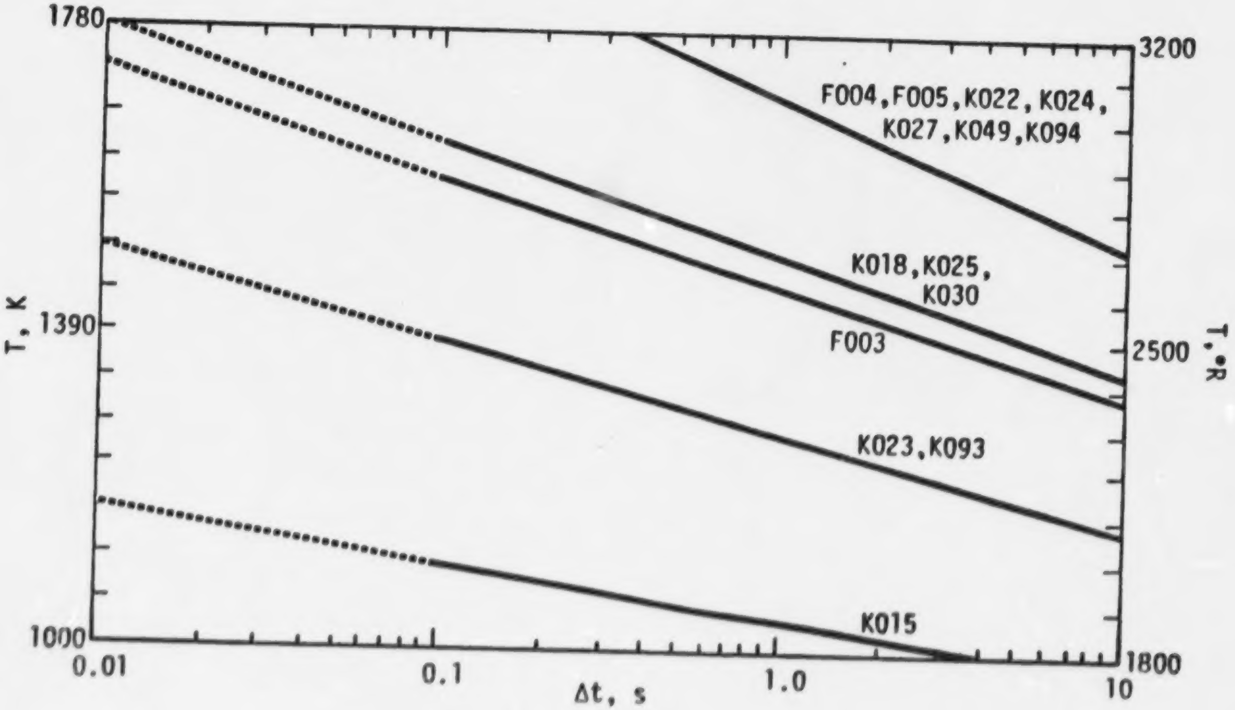

Figure 2-1. Plots of time - temperature requirements for 99.99 percent destruction of selected hazardous waste categories.

TABLE 2-7. SUMMARY OF DATA NEEDED TO EVALUATE THERMAL DESTRUCTIBILITY OF SELECTED HAZARDOUS WASTES

Waste	Approximate heat value,[a] kcal/g	Most conservative compound for calculating kinetic data[b]	A,[c,d] sec^{-1}	E,[c,d] kcal/mol	Physical state[e]	Predominant organic compound,[e] % of total	Geographic location[f]
F003	8.3	Xylene	4.2×10^{12}	77.5	Organic liquid and sludge	Nonhalogenated solvent (25%)	Widespread
F004	6.7	Cresols	(1.0×10^{10})[g]	(70)[g]	Organic liquid and sludge	Nonhalogenated solvent (25%)	Widespread
F005	6.0	Pyridine	(1.0×10^{10})[g]	(70)[g]	Organic liquid and sludge	Nonhalogenated solvent (25%)	Widespread
K015	4.2	Benzyl chloride	1.9×10^{16}	72.6	Organic sludge	Benzyl chloride (2-10%)	
K018	1.8	Hexachlorobutadiene	2.1×10^{12}	77.5	Organic liquid	Heavy chlorinated organics (43%) (hexachlorobenzene, etc.)	Tex., La., N.J., Calif.
K022	7.2	Phenol	(1.0×10^{10})[g]	(70)[g]	Organic sludge	Tars (90%)	Widespread
K023	5.2	Maleic anhydride	1.0×10^{13}	70	Organic liquid	Maleic anhydride (90%)	Pa., Ill., N.J., Calif., La., Tex.
K024	5.2	Phthalic anhydride	(1.0×10^{10})[g]	(70)[g]	Organic sludge	Phthalic anhydride (<50%)	Pa., Ill., N.J., Calif., La., Tex.
K025	6.0	Nitrobenzene	2.1×10^{12}	77.5	Organic sludge	m-Dinitro Benzene (94%)	Miss., Tex., N.J., W.Va., La.
K027	6.0	Toluene diisocyanate	(1.0×10^{10})[g]	(70)[g]	Organic sludge	Polymers and Tars (90%)	Tex., La., Ohio, W.Va.
K030	2.2	Hexachlorobutadiene	2.1×10^{12}	77.5	Organic liquid	Hexachlorobutadiene (34%)	La., Tex., Ky., Kans., Calif.
K049	3.3	Oil	(1.0×10^{10})[g]	(70)[g]	Aqueous sludge	H_2O (40%); Oil (34-43%)	Widespread
K093	5.2	Maleic anhydride	1.0×10^{13}	70	Organic liquid	Phthalic anhydride (<100%)	Ill., Tex., N.J., Puerto Rico, Calif.
K094	5.2	Phthalic anhydride	(1.0×10^{10})[g]	(70)[g]	Organic sludge	Phthalic anhydride (<100%)	Ill., Tex., N.J., Puerto Rico, Calif.

[a] Ref. 2, 3, 6.

[b] Table 3-6.

[c] Table 3-6.

[d] A = Arrhenius pre-exponent frequency factor; E = energy of activation for bond rupture.

[e] Ref. 1.

[f] Ref. 1, 2.

[g] Parenthesis indicate no A, E data were available and worst case conditions were used.

SECTION 3

HAZARDOUS WASTE DESTRUCTION MODEL FOR IDENTIFYING WASTE CATEGORIES DESTRUCTIBLE IN INDUSTRIAL PROCESSES

The destruction of hazardous wastes in an industrial process is primarily dependent on the temperature and residence time profiles of the waste combustion products in the high-temperature furnace. Hence, a knowledge of the temperature-residence time relationship throughout the furnace is essential for estimating the destruction potential of any hazardous waste. A comparison of the time-temperature characteristics of the wastes (developed in Section 2) and the process temperature-residence time profiles should identify the potentially destructible (99.99 percent) hazardous waste.

3.1 PROCESS TEMPERATURE-RESIDENCE TIME PROFILES

3.1.1 Bulk Residence Time Calculations

The computation of bulk residence times for the various processes requires that a flow model be postulated for the gases in the furnace. The plug flow model modified by a degree of mixing serves as a good approximation. This model assumes that there is no longitudinal mixing of the gaseous combustion products along the flow path.[7] Consequently, the temperature, composition, and velocity of the gases are uniform at any chosen cross section of the furnace.

For an isothermal plug flow furnace, the mean residence time (t) is given by the furnace volume (V) divided by the actual gas volumetric flow rate (Q'):

$$t = \frac{V}{Q'} \cdot 60 \qquad (1)$$

The ideal gas law should closely describe the temperature and volume relationship of the gases in the furnace since process operating pressures are low (close to atmospheric) and temperatures are high (significantly higher than the boiling point of the compounds). Any slight error introduced by use of the ideal gas law should be small in relation to the distribution of residence times. Using the ideal gas law, the actual volumetric flow rate (Q') can be computed from the standard volumetric flow rate (Q_s) by correcting for temperature:

$$Q' = Q_s \cdot \frac{T}{273} \qquad (2)$$

where T is in °K

Combining (1) and (2), the mean residence time of an isothermal furnace can be expressed as:

$$t = \frac{16{,}400\ V}{Q_s T} \qquad (3)$$

where t = mean residence time, s

V = furnace volume, m^3

Q_s = standard volumetric flow rate, Nm^3/min (273°K or 0°C)

T = temperature, K

In reality, however, some longitudinal mixing and gas recirculation often occur in the furnaces and result in deviations from total plug flow behavior. Thus, a portion of the gas may follow a faster path and exit the furnace at a time less than t. Experimental measurements have shown that the minimum residence time is approximately 0.5 t.[3] This time is defined as the fast-path residence time ($\bar{t}$).

3.1.2 Incorporation of Temperature-Residence Time Profile

The temperature-time relationship developed in Section 3.1.1 is applicable for isothermal processes only. In an actual furnace, the gas exits at a temperature that is lower than the maximum reaction zone temperature, i.e., the furnace operation is not isothermal. Hence, it is necessary to incorporate the temperature-axial distance profile of the furnace to determine the temperature-residence time relationship for various temperatures in the furnace.

A differential analysis appears to be suitable.[8] The mean residence time dt in an element of volume dV can be expressed as:

$$dt = \frac{dV}{Q'} \qquad (4)$$

Equation 4 is the appropriate differential form of Equation 1.

Further, if A is the cross-sectional area of the furnace (assumed constant), and dx represents an element of axial length in the furnace,

$$dV = A\ dx \qquad (5)$$

Combining Equations 4 and 5,

$$dt = \frac{A\ dx}{Q'} \qquad (6)$$

Noting that Q' is a function of temperature as given by Equation 2,

$$dt = \frac{16{,}400\ A\ dx}{Q_s \cdot T} \qquad (7)$$

The temperature T in the above equation is a function of axial distance. Because detailed temperature-axial distance profiles are rarely available for furnaces used by industrial processes, an approximate solution to Equation 7 can be obtained by assuming a linear gas temperature-axial distance profile between the point of maximum temperature (T_m at distance x_m) and the furnace exit (T_e at distance x_e). The linear profile can be mathematically expressed as:

$$T = \frac{(T_m - T_e)x + T_e x_m - T_m x_e}{(x_m - x_e)} \qquad (8)$$

Substitution of Equation 8 for T in Equation 7 and subsequent integration gives

$$(t - t_m) = \frac{16{,}400\ A}{Q_s} \cdot \frac{(x_m - x_e)}{T_m - T_e} \ln \frac{T}{T_m} \qquad (9)$$

If we further assume that the maximum temperature (T_m) in the furnace occurs very near the entrance to the furnace, i.e., $x_m << x_e$, and noting that Ax_e is the furnace volume, V,

$$(t - t_m) = \frac{16{,}400\ V}{Q_s\ (T_e - T_m)} \ln \frac{T}{T_m} \qquad (10)$$

where $t - t_m$ is in seconds

V is in m^3

Q is in Nm^3/min

T, T_e, T_m are in K

Equation 10 is a simplified expression for the mean residence time of the gas above a given temperature, T, in the furnace. According to Equation 10, the mean residence time of the gas above the furnace exit temperature T_e is:

$$(t_e - t_m) = \frac{16{,}400\ V}{Q\ (T_e - T_m)} \ln \frac{T_e}{T_m} \qquad (11)$$

The fast-path residence time ($\bar{t} - \bar{t}_m$) of the gas above a certain temperature T can be calculated from the mean residence time determined from Equation 10, according to the following equation:

$$(\bar{t} - \bar{t}_m) = 0.5\ (t - t_m) \qquad (12)$$

Use of Equation 10 requires a knowledge of the following parameters for the industrial process/furnace:

- Furnace volume
- Volumetric flow rate of the gases
- Maximum temperature attained in the reaction zone
- Exit temperature of gas from the furnace

An extensive search was conducted to obtain representative data for the parameters for each of the candidate industrial processes. When data on volumetric flow of furnace exit gases were not available, inlet flow rates were used to compute Q, based on the assumption that no major reactions occur in the furnace that might drastically change the volumetric flow rate of the gases.

After the necessary data were obtained, process curves were plotted for each of the candidate industrial processes. These curves comprise plots of $(t - t_m)$ vs. T and $(\bar{t} - \bar{t}_m)$ vs. T, respectively called the mean-path and fast-path process curves.

3.2 PREDICTIONS OF DESTRUCTIBLE HAZARDOUS WASTE CATEGORIES

A prediction of destructible hazardous waste categories can now be made by overlaying the temperature-residence time process curves for each candidate process on the hazardous waste temperature-time plots developed earlier in Section 2. It is assumed that all the hazardous wastes are in the gaseous state by the time (t_m) the maximum temperature (T_m) in the furnace is reached. This assumption has been shown to be valid for the types of hazardous wastes being considered in this study.[3]

The approach towards predicting destructible hazardous wastes in the industrial process is composed of 1) an initial conservative estimate, and 2) an extended conservative estimate.

3.2.1 Initial Conservative Estimate

Essentially, the initial conservative estimate of destructible hazardous waste categories considers only the lowest temperature profile of the process, i.e., T_e corresponding to residence time above T_e. Equation 11 $(t_e - t_m)$ allows computation of the mean residence time above the exit temperature. The fast-path residence time above the exit temperature can then be calculated by use of equation 12 $(\bar{t}_e - \bar{t}_m)$. A horizontal line connecting the points $(t_e - t_m, T_e)$ and $(\bar{t}e - \bar{t}_m, T_e)$ can be drawn on the process curve plots for each process considered. This line is defined as the most conservative line. By overlaying this line on the hazardous waste time-temperature plots, one can make an initial conservative estimate of destructible wastes according to the following guidelines:

- If the hazardous waste plot lies completely below the most conservative line, 99.99 percent destruction of the waste will be achieved.
- If the hazardous waste plot lies completely above the most conservative line, 99.99 percent destruction of the waste will not be reached.
- If the hazardous waste plot lies only partially above or below the most conservative line, 99.99 percent destruction of the waste may only be marginally achieved.

An initial conservative estimate of destructible wastes is not evaluated for industrial processes with a furnace exit gas temperature below 1800°R (the lowest temperature on the hazardous waste plots).

3.2.2 Extended Conservative Estimate

In the industrial processes, the hazardous wastes will be subjected to temperatures above the furnace exit gas temperature, and the rate of destruction will be greater at these higher temperatures. The extended conservative estimate of incinerable hazardous waste categories is developed to account for these higher destruction rates.

The approach to the extended conservative estimate consists of comparing the process curves (plots of $t - t_m$ vs. T and $\bar{t} - \bar{t}_m$ vs. T) with the temperature and times required for thermal destruction of the hazardous wastes. An overlay of the process curves for a candidate industrial process on the hazardous waste plots results in an extended estimate of destructible hazardous waste categories, based on the same guidelines stipulated in Section 3.2.1, but substituting process curves for most conservative line.

Both the initial and the extended conservative estimates can be used to predict those hazardous waste categories that are potentially destructible. This prediction reduces the number of waste categories for which a more extensive evaluation must be undertaken.

3.2.3 Illustrative Example

The following example illustrates the approaches for determining destructible hazardous waste categories in an industrial process. The oil furnace process in the manufacture of carbon black is the candidate process selected.

3.2.3.1 Process Temperature-Time Profiles--

Process parameters:

Furnace volume (V) = 9.63 m^3 (340 ft^3)

Volumetric flow rate of gases (Q) = 105 Nm^3/min (4000 scfm)

Note: Nm^3/min is based on 0°C or 273°K whereas scfm is based on 70°F or 530°R.

Furnace temperatures:

Maximum reaction zone temperature (T_m) = 1670 K (3010°R)

Exit gas temperature (T_e) = 1030 K (1860°R)

Temperature-residence time profiles--Equation 10 provides a way to calculate the mean residence time above any temperature (T) in the furnace, whereas Equation 12 relates the fast-path residence time to the mean residence time. Table 3-1 presents calculated mean and fast-path residence times above a given furnace temperature.

Figure 3-1 shows plots of the mean path and fast-path process curves, i.e., Δt vs. T and $\Delta \bar{t}$ vs. T, overlaid on the hazardous waste time-temperature plots. It also shows the most conservative line connecting the mean-path and fast-path residence times corresponding to exit gas temperature (T_e).

Predictions of destructible hazardous waste categories--By use of the guidelines presented earlier in this section, predictions regarding the potential of the oil furnace process to achieve 99.99 percent destruction of hazardous wastes can be made, based on Figure 3-1. Table 3-2 presents the results. Waste type F003 is shown as a marginal case because it appears to be destructible only under mean-path conditions.

TABLE 3-1. TIME-TEMPERATURE CALCULATIONS FOR THE OIL FURNACE PROCESS IN CARBON BLACK MANUFACTURE

Temperature (T), K (°R)	Mean residence time above T $\Delta t = (t - t_m)$, s	Fast-path residence time above T $\Delta\bar{t} = (\bar{t} - \bar{t}_m)$, s
1670 (3010) (T_m)		
1610 (2900)	0.088	0.044
1560 (2800)	0.17	0.085
1450 (2600)	0.34	0.17
1330 (2400)	0.53	0.27
1220 (2200)	0.74	0.37
1110 (2000)	0.96	0.48
1030 (1860) (T_e)	1.13	0.56

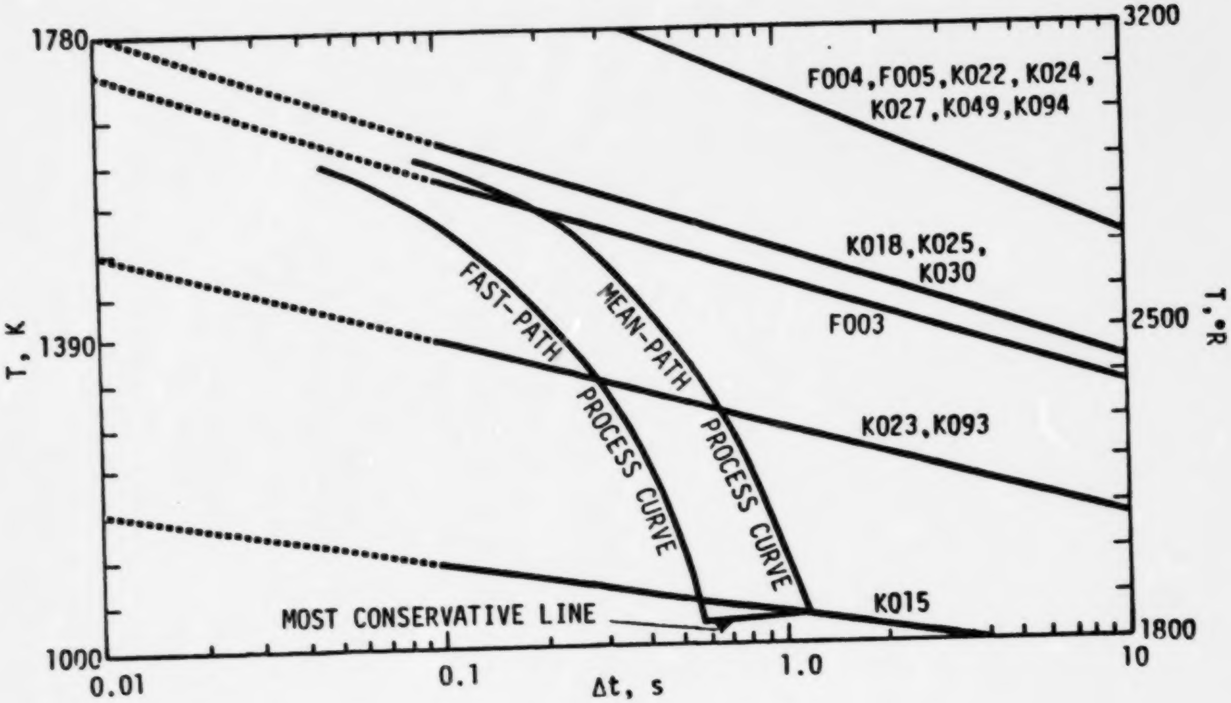

Figure 3-1. Hazardous waste destructibility predictions for the oil furnace process in carbon black manufacture.

TABLE 3-2. FEASIBILITY OF OIL FURNACE PROCESS (CARBON BLACK) FOR THERMAL DESTRUCTION OF HAZARDOUS WASTES

Type of conservative estimate	Hazardous waste type													
	F003	F004	F005	K015	K018	K022	K023	K024	K025	K027	K030	K049	K093	K094
Initial	No	No	No	No	No	No	No	No	No	No	No	No	No	No
Extended	Maybe	No	No	Yes	No	No	Yes	No	No	No	No	No	Yes	No

SECTION 4

PROCESS ASSESSMENT

All of the major industrial processes in the United States were reviewed, from both a technical and availability standpoint, for selection of the most promising candidates for hazardous waste destruction.

The initial listing of approximately 100 processes was based on operating temperature and included any major process with an operating temperature of greater than 649°C (1200°F). (See Appendix C.) It includes processes from the metallurgical, chemical, and mineral industries and sludge and waste incinerators. Each of these industries was then screened against the criteria listed in Table 4-1 to eliminate from further consideration those industries that show little potential for effective hazardous waste disposal.

TABLE 4-1. SCREENING CRITERIA FOR POTENTIAL HIGH-TEMPERATURE PROCESSES FOR THE DESTRUCTION OF HAZARDOUS WASTE

- Compatibility of process
  - Thermal destruction conditions: temperature and residence time (turbulence not considered)
  - Product quality
  - Potential for fugitive emissions
- Number of facilities
- Geographic matching of industry location and waste generators

Gas residence time within the process during high-temperature conditions was an important consideration; the lower the process temperature, the longer is the residence time required for 99.99 percent thermal destruction. Turbulence, the other condition necessary for combustion, was not considered because information on this parameter is generally sparse. Residence time and product quality considerations eliminated organic and miscellaneous chemical manufacturing processes from consideration because high temperatures are often attained in the reactors, but residence times are quite short.

Product quality, both actual and perceived, was another important consideration. Destroying hazardous waste in a steel furnace, for example, could increase trace elements in the steel and affect its physical properties, and in all cases, hazardous waste disposal was considered secondary to product quality. This criterion eliminated processes such as basic oxygen and electric arc furnaces in the steel industry because these processes produce a high-quality steel that cannot tolerate residues from hazardous waste destruction. This criterion also affected chemical manufacturing, food processing (human and animal consumption), fertilizer manufacturing, and petroleum refining processes.

The more potential a process has for fugitive emissions, the less likely it is to be suitable for hazardous waste disposal. Raw materials handling procedures also affect the potential for a process to generate fugitive emissions and its suitability for hazardous waste disposal. In a sintering process at an iron and steel mill, for example, open conveyors are used to transport raw materials to the pug mill (mixing device) and to the sinter strand, which is also open. The major modifications to the materials-handling system that would be required to correct this high potential for fugitive emissions and the short residence time at the maximum temperature of about 1210°C (2200°F) resulted in the elimination of the iron and steel sintering process from further consideration. The fugitive emissions potential and short residence times, coupled with their location in highly populated areas, also eliminated municipal solid waste incinerators from the list of possible processes.

The number of facilities available in areas of high hazardous waste generation was another major consideration. For example, specialty processes that are located in only a few widely scattered places or developing processes that are currently operational at only a few sites were not considered. The processes selected for detailed analysis were those with the potential for disposing of significant quantities of hazardous wastes.

Table 4-2 lists those industries and processes that remained after the screening criteria had been applied. These processes were evaluated in more detail by use of the hazardous waste destruction model discussed in Section 3. The process assessments are presented alphabetically by industry in Subsections 4.1 through 4.10.

4.1 BRICK AND TILE INDUSTRY

The brick and tile industry includes those establishments engaged primarily in the manufacture of common brick, refractory brick, and structural clay tiles. The manufacturing steps involved are blending of the raw material, grinding, screening, forming, and in some cases, drying. The final step consists of heating the ware (brick or tile) in either a tunnel kiln or a periodic kiln. This process is also known as firing or burning of the ware. Figure 4.1-1 is a generalized flow diagram of a brick and tile plant. Several changes occur during the firing process, including the liberation of both free and combined water, the combustion of organic matter, the decomposition of impurities, and the bonding of solid clay particles.[9] Table 4.1-1 presents common clay impurities and their respective breakdown temperatures. Corresponding changes in physical properties accompany the alterations in the composition and

TABLE 4-2. INDUSTRIES AND PROCESSES SELECTED FOR FURTHER HAZARDOUS WASTE DESTRUCTION EVALUATION

Industry	Process or furnace	Exit and maximum temperatures, °C	Residence time (seconds, unless otherwise noted)[a]
Brick	Tunnel Kiln	260-1180	4.3
Carbon black	Oil furnace process	870-1400	1.1
Primary copper	Reverberatory furnace	1300-1400	2.2
Primary lead	Blast furnace	700-1200	5.9
Primary zinc	Multiple-hearth roaster	200-980	>10
	Suspension roaster	930-1010	>10
	Fluidized-bed roaster	950-1740	>10
Iron and steel	Blast furnace	1100[b]-1870	1.1[c]
	Open hearth furnace	1200-1800	2.0
Lime	Long rotary kiln	680-1900	8.3
	Short rotary kiln with stone preheater	1160-1840	7.6
Lightweight aggregate	Rotary kiln		
Glass	Melting furnace	620-1480	4.1
Sewage sludge	Fluid-bed furnace	760-870	1.4
	Multiple-hearth furnace	480-980	0.5
Hazardous waste incineration[d]	Rotary kiln	820-1600	2.0 s to 2 h[e]
	Liquid injection	700-1650	0.5 to 2

[a] Residence time above the greater of the exit temperature or 760°C.

[b] Represents estimated temperature at the top of the combustion zone in the blast furnace.

[c] Residence time has been calculated using 33 percent of the total furnace volume.

[d] Included for comparison only.

[e] The residence time for solids and sludges can be adjusted.

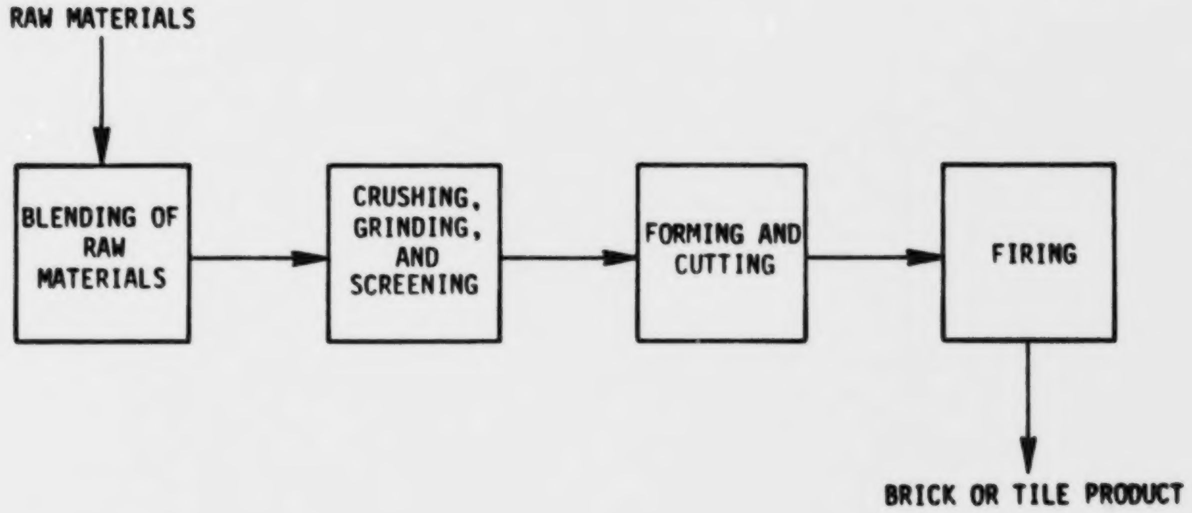
RAW MATERIALS
BLENDING OF RAW MATERIALS
CRUSHING, GRINDING, AND SCREENING
FORMING AND CUTTING
FIRING
BRICK OR TILE PRODUCT

Figure 4.1-1. Generalized flow diagram of a brick and tile plant.

TABLE 4.1-1. BREAKDOWN TEMPERATURES OF CLAY IMPURITIES[9]

	Temperature,	
	°C	°F
$FeS_2 + O_2 \rightarrow FeS + SO_2$	350-450	660-840
$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2$	500-800	930-1470
$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$	560-775	1040-1430
$C + O_2 \rightarrow CO_2$	350	660
$S + O_2 \rightarrow SO_2$	250-920	480-1690
$CaCO_3 \rightarrow CaO + CO_2$	600-1050	1110-1920
$MgCO_3 \rightarrow MgO + CO_2$	400-900	750-1650
$FeCO_3 + 3O_2 \rightarrow 2Fe_2O_3 + 4CO_2$	800	1470
$CaSO_4 \rightarrow CaO + SO_3$	1250-1300	2280-2370

mineralogical constitution of the clay product. Most notable are true specific gravity, porosity, volume, strength, and hardness.[10]

4.1.1 Process Descriptions

4.1.1.1 Tunnel Kilns--

Tunnel kilns are used in most modern brick and tile plants. Figure 4.1-2 presents a typical configuration. The product is loaded onto a car and charged into the left end of the kiln. As the car progresses along the length of the kiln, it passes through zones of increasing temperature. In most cases, the kiln has two sets of burners. The main (or upper) fuel-fired burners are located along the middle section of the kiln and provide the bulk of heat necessary for firing.[11] Secondary (or lower) burners are located along the length of the kiln between the preheating zone and the firing zones. Air is passed through the kiln countercurrently to the movement of the ware.[11] The exact amount of excess air varies with the desired product specifications.[10] As the ware leaves the combustion zone, cold air forced in from the right end of the kiln passes over the charge cooling it by countercurrent heat exchange. Some of this air is withdrawn for use as preheated primary combustion air; the remaining air continues to the left, enters the combustion zone, mixes with the combustion gases, and then passes over the incoming charge, where it loses much of its heat. Air locks located at both ends of the kiln prohibit flow conditions from being disturbed by the entrance or exit of cars.[11]

Processing is continuous, and the average tunnel kiln produces 100,000 bricks per day.[12] The inside dimensions of a typical kiln are 98 m (321 feet) long by 3.4 m (11.2 feet) wide by 1.5 m (4.9 feet) high.[12] Historically, tunnel kilns were fired with natural gas; however, oil, coal, or sawdust are often used today. These kilns generally consume approximately 2326 to 2791 kJ/kg (1000 to 1200 Btu/lb) of brick; newer kilns are

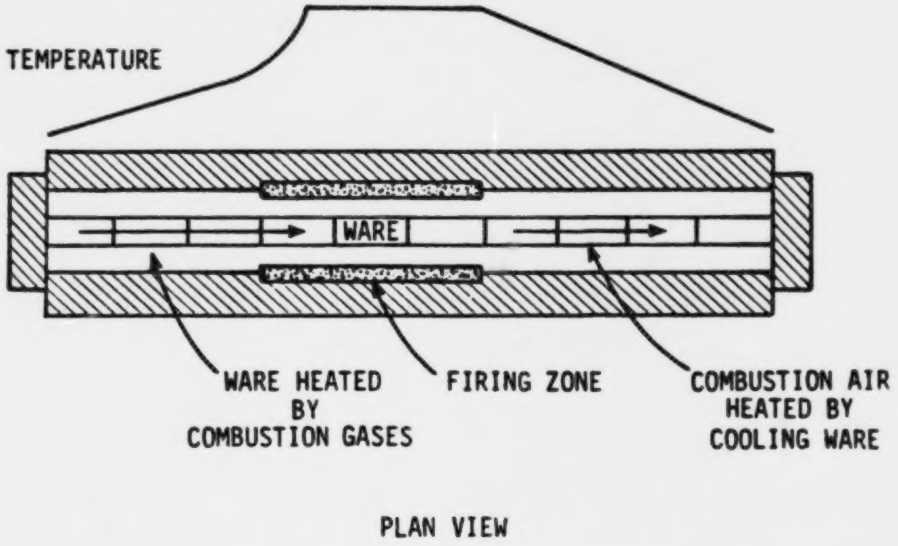
TEMPERATURE
WARE
WARE HEATED BY COMBUSTION GASES
FIRING ZONE
COMBUSTION AIR HEATED BY COOLING WARE
PLAN VIEW

Figure 4.1-2. Diagram of a tunnel kiln.[11]

designed to consume 1860 kJ/kg (800 Btu/lb). An average brick weighs 2.2 kg (5 lb).[12]

4.1.1.2 Periodic Kilns--

Because of its high energy and labor requirements, the periodic (or beehive) kiln is in the process of being phased out.[12] The downdraft periodic kiln is a permanent brick structure with several fireholes through which fuel is fired.[13] The hot combustion gases are drawn over and through the bricks by underground flues. A 2-week cycle is required to fire, cool, and discharge the product.[10] Fuel is burned approximately 50 percent of the time. Although fuel efficiency is not as high as in a tunnel kiln, the uniform temperature distribution throughout the periodic kiln leads to a high-quality product. In most cases it is used for small-scale production.[11]

4.1.2 Process Assessment for Hazardous Destruction

Because of its wide application, relatively long residence time, and moderately high-temperature range, the tunnel kiln appears to offer an alternative for disposing of hazardous wastes. The periodic kiln, on the other hand, is in the process of being phased out and therefore would not provide a long-term solution to this problem.

4.1.2.1 Technical Factors--

Compatibility of hazardous wastes with process fuels--Most new tunnel kilns are being designed to burn more than one fuel type. This dual fuel design would be advantageous if hazardous wastes were to be introduced. Kilns designed to fire only solid or gaseous fuels would have to be retrofitted to accept a liquid waste. Installation of a liquid burner/atomizer system with the appropriate pump and piping would suffice. The waste burners should be located along the upper row near the burner firing the main fuel. Appendix A provides a more detailed discussion on the requirements for equipment and handling procedures necessary to fire hazardous wastes.

Graphic determination of suitable waste categories--The bulk residence time (8.0 seconds, based on a maximum temperature) and temperature range [260° to 1180°C (500° to 2150°F)] of a typical tunnel kiln indicate that destruction of hazardous wastes in this furnace is feasible. A typical brick and tile tunnel kiln processes 100,000 bricks or an equivalent tonnage per day.[12] Inasmuch as burners are only located between the preheating and firing zones, a "working" furnace volume had to be calculated. This working volume more accurately reflects the area where hazardous waste destruction would take place. Based on a typical temperature profile within the kiln, an average working volume of 335 m^3 (11,833 ft^3) was calculated.[12] In addition, the kiln has an average volumetric flow rate of 473 Nm^3/min (18,000 scfm).[12]

Figure 4.1-3 plots the change in residence time for mean (Δt), and fast ($\Delta \bar{t}$) path process curves of a tunnel kiln. These plots are overlaid on the hazardous waste curves to determine which hazardous waste categories are destructible, given the kiln's time-temperature relationship. Based on data from this graph, Table 4.1-2 provides predictions regarding the ability of a typical tunnel kiln to destroy (99.99%) the selected hazardous wastes. Because the exit gas temperature falls below the lowest temperature in the graph (Figure 4.1-2), the conservative process line is not shown. Based on the extended case, it appears that K015, K023, and K093 could be 99.99 percent destroyed.

TABLE 4.1-2. APPLICABILITY OF THE BRICK AND TILE TUNNEL KILN FOR THERMAL DESTRUCTION OF HAZARDOUS WASTES

K015	K023, K093	F003	K018, K025 K030	F004, F005, K022, K024 K027, K049, K094
Yes	Yes	No	No	No

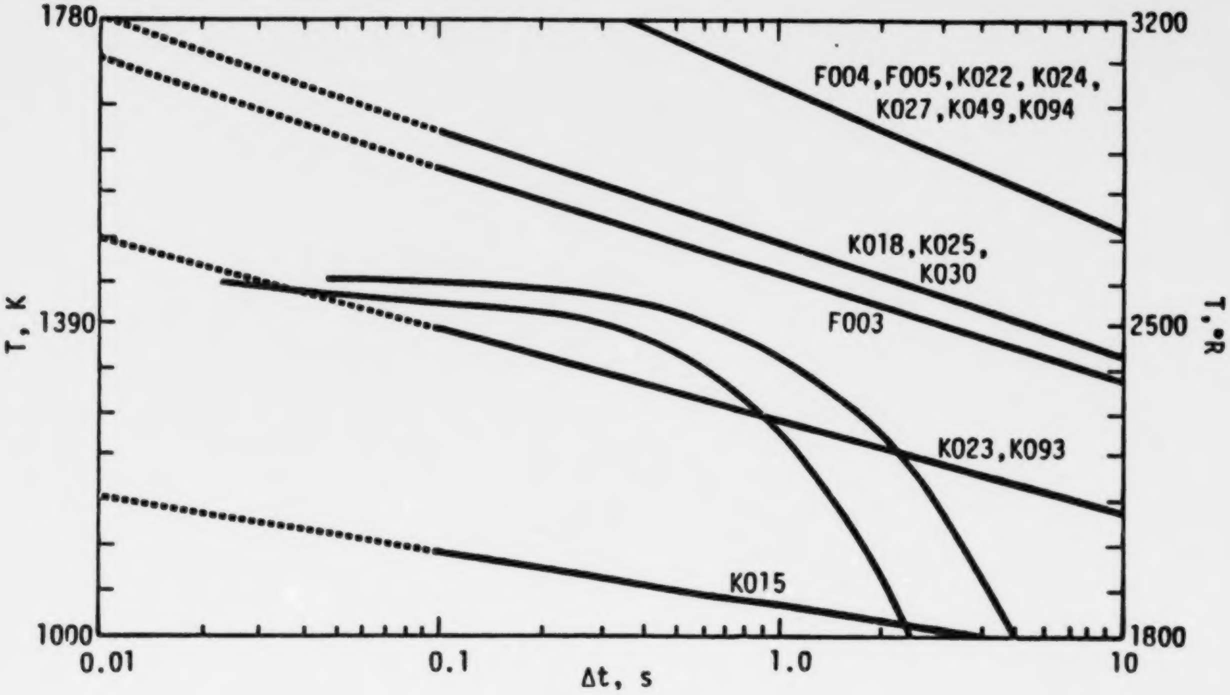

Figure 4.1-3. Hazardous waste destructibility for the brick and tile tunnel kiln.

Effects on product quality and product application--Almost all (97 percent) of the output from the brick and tile industry is purchased for construction.[14] Because of the bulk and weight of brick and tile products, markets tend to be regional in character. Intra-product competition is based as much on specialty features, such as style, finishes, and color, as on price. Any effect on these features resulting from the destruction of hazardous waste would be a major detriment.

Studies are being conducted on the impact of substituting municipal and industrial sludges for a portion of the clay prior to firing the bricks. The sludge burns during firing and releases heat; this leaves tiny bubbles in the bricks which may enhance their insulating capability. Though not as strong as clay bricks, these bricks made with sludge reportedly meet the standards of strength set by the American Society for Testing and Materials.[15] Whereas studies indicate that destroying hazardous organic wastes in the tunnel kiln might have some impact on the brick and tile, it may not seriously degrade product quality.[15]

Changes in the kiln's atmosphere resulting from the incineration of hazardous organic wastes could discolor the brick and tile. Color is dependent on the atmosphere of the kiln (oxidizing and reducing), kiln temperature, and the impurities within the raw materials. The pink color often associated with brick used for residential construction comes from iron impurities.[10] Normally, the iron impurities present in the clay (whether oxides, carbonates, sulfides, or sulfates) are oxidized to ferric oxide (Fe_2O_3), which generally gives rise to various shades of yellow or red.[10] Occasionally the atmosphere within the kiln may not be oxidizing, however, in which case lower oxides such as magnetite (Fe_3O_4) or ferrous oxide (FeO) may be formed and give rise to black or blue-black colors. The introduction and subsequent oxidation of hazardous wastes could alter the atmosphere of the kiln in the immediate area of the ware, and a lack of excess oxygen or a reducing atmosphere may cause this darker

Based on a continuous output of 100,000 bricks/day in a typical tunnel kiln, up to 2530 kg (5600 lb) of hazardous wastes could be destroyed per day. Assuming 260 days of operation per year, a tunnel kiln's annual hazardous waste disposal rate can be estimated as follows:

$$2490 \text{ kg/day} \times 260 \text{ days/yr} \times \text{Mg}/1000 \text{ kg} = 647 \text{ Mg/yr}$$

Trends in process fuel consumptions--Newer kilns are being designed to accept more than one fuel type; for example, either sawdust and/or oil. These new kilns are also significantly more fuel-efficient; they consume about 1860 kJ/kg (800 Btu/lb) of brick compared with the current average of 2790 kJ/kg (1200 Btu/lb).[12] The trend toward multiple fuels and higher fuel efficiency is likely to continue in future design modifications and should increase the kiln's potential for destroying hazardous waste.

4.1.2.2 Geographic Matching of Industry Locations and Waste Generators--

Figure 4.1-4 shows the distribution of domestic brick and tile plants by state. It should be noted that the majority of these plants use kilns of the small, batch type, which are unsuitable for destroying hazardous wastes. No firm numbers were available, but it is estimated that approximately 130 of the total 466 brick and tile plants utilize tunnel kilns.

Table 4.1-3 presents the SIC code and geographic distribution of each destructible waste category. The states specifically identified as generating these wastes (California, New Jersey, Louisiana, Pennsylvania, Illinois, Puerto Rico, and Texas) contain 30 percent of the total operating brick and tile plants.

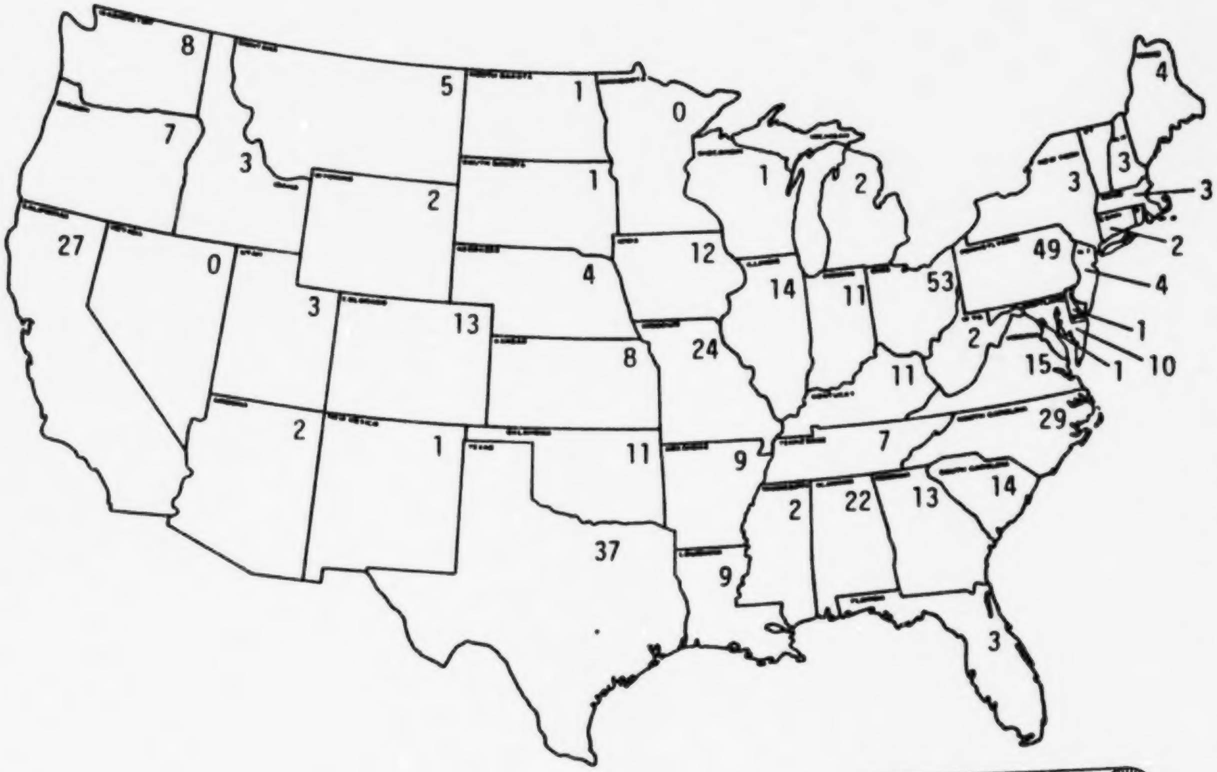
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Figure 4.1-4. Geographic distribution of U.S. structural clay products plants (1973.)[16,17,18]

TABLE 4.1-3. SIC CODES AND GEOGRAPHIC DISTRIBUTION OF INDUSTRIES GENERATING HAZARDOUS WASTE DESTRUCTIBLE IN BRICK AND TILE TUNNEL KILNS[1,19]

Category	SIC code of generating industry	Geographic location
K015		Two plants (locations not known)
K023	2869	Richmond and El Sequendo, California; Kearney and Bridgeport, New Jersey; Baton Rouge, Louisiana; Bridgeville and Neville Island, Pennsylvania; Cicero and Millsdale, Illinois; Texas City, Texas
K093	2869	Illinois, Texas, New Jersey, Puerto Rico, California

4.1.2.3 Environmental Factors--

Impact on air pollution control devices--Atmospheric emissions from tunnel kilns consist of total suspended particulates (TSP), sulfur dioxide (SO_2), carbon monoxide (CO), nitrogen oxides (NO_x), hydrocarbons (HC), and in some cases, fluorides (HF), all of which can be detrimental to one's health. The TSP, SO_2, CO, and NO_x are primarily products of combustion and thus a function of the fuel used.[13,14] Some raw materials also contain a relatively high quantity of organic or sulfur-bearing impurities, which could increase these emissions. Kiln temperatures must reach 1370°C (2500°F) or greater for sulfur dioxide to be emitted from impurities within the brick.[13]

Certain clays contain fluorine as an impurity. One of the most common fluorine-containing impurities in clay is fluorite or fluorspar (CaF_2).[9] During firing, this impurity reacts to form hydrogen fluoride (HF), which can hydrolize at flue gas temperatures to form hydrofluoric acid mist. Table 4.1-4 shows emissions factors for tunnel kilns that fire oil, coal, or natural gas.

TABLE 4.1-4. EMISSION FACTORS FOR A TUNNEL KILN[13]
kg/Mg (lb/ton)

	TSP	SO_2	CO	HC	NO_x	HF
Gas-fired	0.02 (0.04)	Neg[a]	0.02 (0.04)	0.01 (0.02)	0.08 (0.15)	0.5 (1.0)
Oil-fired	0.3 (0.6)	2.0 (4.0)	Neg[a]	0.05 (0.1)	0.55 (1.1)	0.5 (1.0)
Coal-fired	0.5 (1.0)	3.6 (7.2)	0.95 (1.9)	0.3 (0.6)	0.45 (0.9)	0.5 (1.0)

[a] Negligible.

Air pollution control devices are generally tailored to the specific contaminants generated from impurities in the clay or fuel. Most kilns do not have pollution control equipment because they use a clay with few impurities or fire with natural gas. At the opposite end of the spectrum, a few plants may use a wet scrubber to control HF and SO_2 emissions and an afterburner to eliminate hydrocarbon emissions. If currently pending New Source Performance Standards are promulgated, most plants built after 1982 will be required to incorporate these control devices into their design.

Plants considering the destruction of hazardous wastes will require both a high-energy wet scrubber to eliminate gaseous emissions and an afterburner to eliminate products of incomplete combustion. Depending on the increases in pollutant loading and extent of existing control equipment, an adjustment in control devices may be all that some plants require, whereas others may need a complete retrofitting of suitable controls.

A potential exists for trace quantities of incomplete combustion products to escape into the stack gases. The afterburner should effectively destroy these compounds, but the actual behavior of hazardous wastes and their associated products of incomplete combustion need to be investigated further. This could be accomplished by conducting a test burn to determine the exact environmental impact associated with thermally destroying specific hazardous wastes in a tunnel kiln.

4.1.2.4 Institutional Factors--

Although the literature does not actually address the destruction of hazardous wastes in these kilns, private companies have been conducting their own studies. Preliminary results from one such study show that tunnel kilns are capable of destroying certain types of organic hazardous waste.[20] Because of the confidential nature of these tests, the specific wastes destroyed and other test data were not available. The fact that these studies have been made, however, indicates an interest on the part of industry. Energy requirements in the brick and tile industry are quite high, and there is a prevailing interest in reducing their energy-related expenditures, either directly by a reduction in the amount of conventional fuel required, or indirectly by offsetting these costs by a disposal fee.

Because many brick and tile plants are located near metropolitan areas, the impact of a waste spill or process failure could be great. Consequently, these kilns must be proven to be an effective and environmentally sound method for disposing of these wastes to prevent adverse impacts on the surrounding community.

4.2 CARBON BLACK INDUSTRY

4.2.1 Process Descriptions

Carbon black can be manufactured by various processes ranging from primitive ones to continuous, high-capacity systems with sophisticated designs and control equipment.[21] The basic reaction by which it is produced may be represented by the following equation:[22]

$$C_nH_m \rightarrow n\ C + \frac{m}{2}\ H_2 \pm H_R \text{ (heat of reaction)}$$

The type of hydrocarbon feedstock used varies with the process employed, and this feedstock determines whether the reaction is endothermic or exothermic.

About 94 percent of domestic carbon black production is produced by the oil furnace process. The thermal process is next in popularity. Table 4.2-1 presents the latest estimate of the capacities of U.S. carbon black plants.

4.2.1.1 Oil Furnace Process--

The oil furnace process involves the incomplete combustion and cracking of a liquid hydrocarbon feedstock at temperatures of approximately 1370°C (2500°F) and 20 to 50 percent excess air to produce an aerosol of carbon particles.[23] Figure 4.2-1 presents a detailed flow diagram of a typical process.

The input materials to the reactor include a preheated oil feedstock, preheated air, and natural gas for heat and product quality control. The preferred feedstocks are high in aromaticity and contain low levels of asphaltenes, sulfur (<3%), and alkali metals. Refinery byproduct residual tars and decant oil from gasoline production are commonly used as feeds. Because the decomposition of heavy aromatic feedstocks in the furnace is slightly endothermic, a considerable amount of energy is required to vaporize and heat the feedstock to reaction temperatures.

Primary quenching with water reduces the temperature of the gaseous effluent from the reactor to approximately 538°C (1000°F). Secondary quenching further reduces the temperature of the gas to less than 260°C (500°F) before it enters the fabric filters. Carbon black, in light fluffy form, is separated in the filters and conveyed to micropulverizers that discharge into a surge tank. The off-gases are burned in a CO boiler, incinerator, or

TABLE 4.2-1. UNITED STATES CARBON BLACK CAPACITY, 1976[21]

Manufacturer	Capacity, 10^3 Mg (10^3 tons)	
	Oil furnace process	Thermal process
Ashland Chemical	304 (335)	
Arkansas Pass, Texas	68 (75)	
Baldwin, Louisiana	116 (128)	
Belpre, Ohio	45 (50)	
Mojave, California	27 (30)	
Shamrock, Texas	48 (53)	
Cabot Corporation	425 (468)	
Big Spring, Texas	113 (125)	
Franklin, Louisiana	91 (100)	
Pampa, Texas	29 (32)	
Parkersburg, West Virginia	74 (82)	
Ville Platte, Louisiana	118 (130)	
Cities Service	343 (378)	
Conroe, Texas	44 (48)	
El Dorado, Arkansas	37 (41)	
Eola, Louisiana	32 (35)	
Franklin, Louisiana	71 (78)	25 (28)
Hickok, Kansas	23 (25)	
Mojave, California	24 (26)	
Moundsville, West Virginia	71 (78)	
Seagraves, Texas	41 (45)	
Continental Oil	194 (214)	
Bakersfield, California	35 (39)	
Ponca City, Oklahoma	61 (67)	
Sunray, Texas	43 (47)	
Westlake, Louisiana	54 (60)	
J. M. Huber Corporation	179 (197)	19 (21)
Baytown, Texas	117 (129)	
Borger, Texas	62 (68)	
Phillips Petroleum	219 (241)	
Borger, Texas	130 (143)	
Orange, Texas	52 (57)	
Toledo, Ohio	36 (40)	
Richardson Company	95 (105)	
Addis, Louisiana	45 (50)	
Big Spring, Texas	50 (55)	
Thermatomic Carbon		
Sterlington, Louisiana[a]		59 (65)
Total	1938	114

[a] Plant closed in 1977.

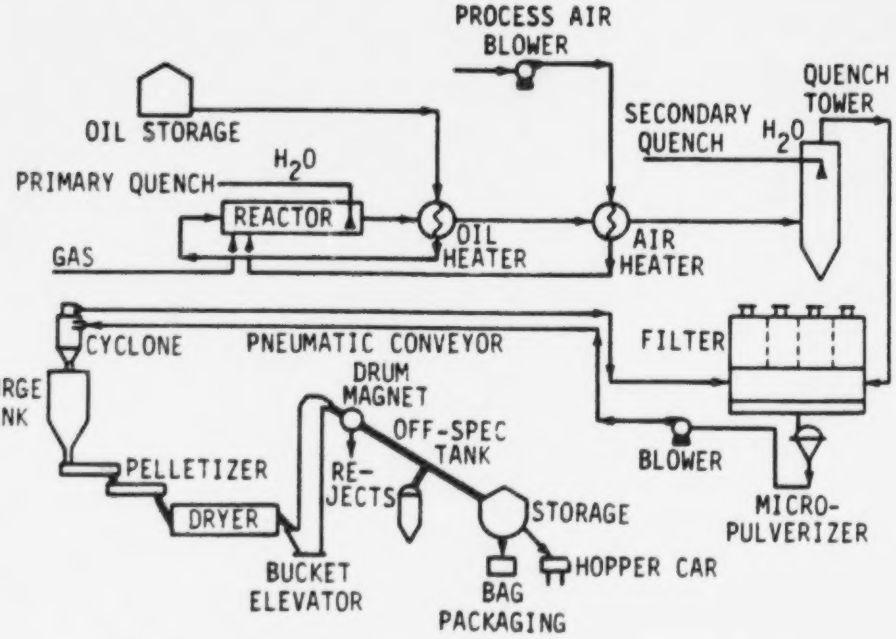
PROCESS AIR BLOWER
OIL STORAGE
QUENCH TOWER
SECONDARY QUENCH
H_2O
PRIMARY QUENCH
H_2O
REACTOR
OIL HEATER
AIR HEATER
GAS
CYCLONE
PNEUMATIC CONVEYOR
FILTER
SURGE TANK
DRUM MAGNET
OFF-SPEC TANK
BLOWER
PELLETIZER
REJECTS
DRYER
STORAGE
MICRO-PULVERIZER
BUCKET ELEVATOR
BAG PACKAGING
HOPPER CAR

Figure 4.2-1. Flow diagram of oil furnace process.[21]

flare to reduce emissions of CO, hydrocarbons, and H_2S. If a boiler is used, heat is recovered as steam.

As shown in Table 4.2-2, different grades of carbon black can be produced by changing reactor temperatures and residence times.

TABLE 4.2-2. TIME-TEMPERATURE CONDITIONS IN CARBON BLACK REACTORS

Black grade	Residence time, s	Temperature, °C (°F)
Thermal (N990)	10	1210-1340 (2200-2450)
SRF (N700 series)	0.9	1400 (2550)
HAF (N300 series)	0.031	1540 (2800)
SAF (N100 series)	0.008	1790 (3250)

4.2.1.2 Thermal Process--

The thermal process involves decomposition of a gaseous hydrocarbon feed by thermal cracking at 1320° to 1540°C (2400° to 2800°F) in the absence of air to yield carbon and hydrogen. Natural gas is used as the feedstock. The product stream from the cracking chamber is filtered to remove carbon black, and the exit gas is burned to generate heat for additional cracking.

4.2.2 Process Assessment for Hazardous Waste Destruction

Of the two processes discussed, the oil furnace process was selected for further evaluation for thermal disposal of hazardous wastes. The thermal decomposition process was not investigated further mainly because of the limited number of these facilities.

4.2.2.1 Technical Factors--

Compatibility of hazardous wastes with process fuel--Most of the waste types being considered for this study are aromatic in nature and hence excellent candidates for disposal by the oil furnace process.

Graphical determination of suitable waste categories--Residence times and temperatures cited for SRF and thermal grades of carbon black appear to be feasible for hazardous waste destruction, whereas the residence times for HAF and SAF grades are too short for waste destruction purposes.

For example, based on the conditions for manufacture of SRF grade carbon black presented in Table 4.2-2:

Residence time at maximum temperature of 1420°C (2550°F) = 0.9 s

Therefore, a gas flow rate of 105 Nm^3/min (4000 $scfm^3$) will require a furnace with a volume of 9.63 m^3 (340 ft^3).

Based on computations of t (mean residence time) and $\bar{t}$ (fast-path residence time) for several temperatures between the maximum temperature [1400°C (2550°F)] and the exit gas temperature [760°C (1400°F)], values are obtained for Δt and $\Delta\bar{t}$. Figure 4.2-2 shows plots of Δt and $\Delta\bar{t}$ versus T (mean- and fast-path process curves) overlaid on the hazardous waste plots to determine destructible hazardous waste categories.

Table 4.2-3 presents predictions regarding the potential of the oil furnace process to achieve 99.99 percent destruction of the hazardous wastes. It appears that the wastes in categories F003, K015, K023, and K093 can be destroyed at the conditions prevailing in the furnace. Waste category F003 is shown as being marginal because these wastes appear to be destructible only under mean-path conditions. High turbulence in the furnace would enhance the destruction of these wastes.

TABLE 4.2-3. FEASIBILITY OF OIL FURNACE PROCESS (CARBON BLACK) FOR THE THERMAL DESTRUCTION OF HAZARDOUS WASTES

Hazardous waste type													
F003	F004	F005	K015	K018	K022	K023	K024	K025	K027	K030	K049	K093	K094
Maybe	No	No	Yes	No	No	Yes	No	No	No	No	No	Yes	No

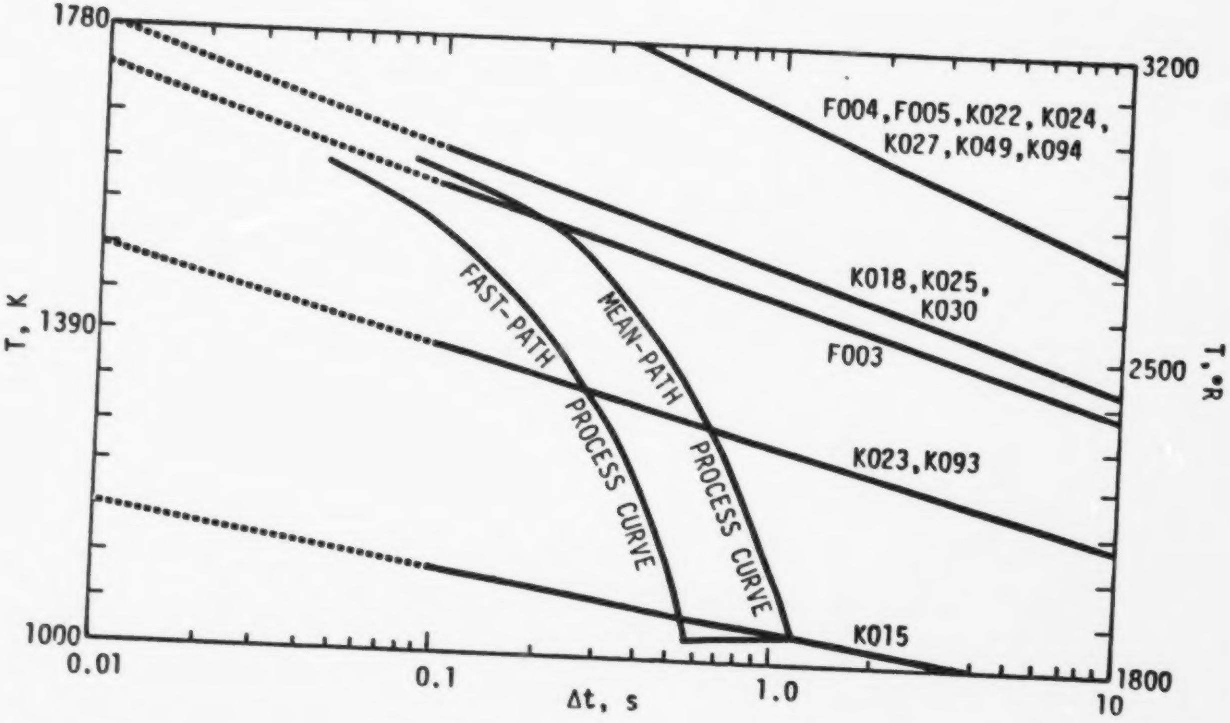

Figure 4.2-2. Hazardous waste destructibilty predictions for the oil furnace process in carbon black manufacture.

Effects on product quality and product application--Because carbon black has a potential for adsorbing gaseous hydrocarbons,[24] some of the hazardous components in the waste may be adsorbed on the surface of the carbon black particles. It is difficult to predict the extent of adsorption of various hazardous components, and test burns would be necessary to determine levels of toxic substances that could be associated with the product.

About 93 percent of the carbon black produced in the United States is consumed by the rubber industry, primarily for use as a reinforcing agent in rubber tires.[24] Contamination of the product should not prevent the use of the carbon black process for destroying hazardous wastes. Tests would be required, however, to ensure that any product contamination would not affect the tensile strength or elasticity and thus the integrity of the product. Secondary uses of carbon black are in inks and paints, and waste destruction is not expected to have any detrimental effect on the quality of these products, either.

Impact on process hardware--The design and construction features of reactors employed for carbon black manufacture are determined by economics and product specifications.[21] Furnace reactors have undergone substantial design changes during the last decade to give higher turbulence, rapid mixing of reactant gases and feedstock, and increased capacity. Refractory-lined metal construction appears to be a notable feature in the latest reactor designs. Inasmuch as these furnaces are designed to accept a fairly wide variety of oil feedstocks (e.g., byproduct residual tars and decant oil from gasoline production), combustion of compatible liquid wastes should not have any deleterious effect on process hardware. Destruction of highly halogenated hazardous wastes, however, may decrease the useful life of the refractory lining.

Acceptable amounts of hazardous waste feed--Operating parameters for furnace processes vary from plant to plant and, within a given plant, depend on the grade of product manufactured.

Typical reactor feed rates and carbon black production rates are as follows:[23]

Rate of feed oil:	757 liters/h (200 gal/h)
Rate of air supplied:	6660 m^3/h (235,000 ft^3/h
Rate of natural gas supplied:	623 m^3/h (22,000 ft^3/h)
Rate of carbon black production:	390 kg/h or 0.52 kg/liter (860 lb/h or 4.3 lb/gal oil)
Yield of carbon black (lb of product per 100 lb of carbon in feedstock:	60 percent

Based on the assumption that the hazardous wastes will represent 10 percent of the volumetric flow rate of feed oil to the furnace, the hazardous waste feed rate will be 76 liters/h. Since the wastes have an average density of 0.95 kg/liter (7.92 lb/gal),[5] the feed rate amounts to about 73 kg/h (160 lb/h) of hazardous waste feed.

Assuming 24 liters/day of process operation 260 days/yr, the amount of disposable hazardous wastes that could be processed in a typical reactor is calculated as follows:

73 kg/h x 24 h/day x 260 days/yr x 1 Mg/1000 kg
= 456 Mg/yr

Provisions for waste introduction--The physical compatibility of the wastes and the oil feedstock appears to be good; therefore, the wastes could be blended with the oil and then preheated and atomized before they enter the furnace. No retrofit problems are anticipated.

Projected trends in process fuel--Recent trends in carbon black production include more emphasis on the furnace process as a result of advances in furnace technology that allow a wide range of carbon blacks to be produced.[24] Hence, it appears that oil (typically highly aromatic petroleum fractions) will be the predominant fuel in the carbon black industry in the future.

4.2.2.2 Geographic Matching of Industry Locations and Waste Generators--

Categories of wastes that were shown to be destructible (in the previous section) are F003, K015, K023, and K093. Table 4.2-4 identifies the SIC code and geographic distribution of the industries generating these destructible wastes. Figure 4.2-3 shows the distribution of carbon black manufacturing plants in the United States. No SIC code is associated with F003 because this waste is generated by nonspecific sources. Two of the selected destructible waste categories (K023, K093) are generated primarily in Texas, California, and New Jersey. Table 4.2-1 (presented earlier) and Figure 4.2-3 reveal that the states of Texas and California account for a substantial fraction of total domestic carbon black production. Hence, the geographic matching of the industry and waste generator locations for waste types K023 and K093 appears to be excellent. This makes the carbon black industry even more attractive for thermal disposal of the candidate hazardous wastes because the shorter distances between waste generators and industry location reduces transportation costs and lessens possible hazards resulting from transport.

4.2.2.3 Environmental Factors--

Impact on air pollution control devices--Suspended carbon black particles usually are collected in control devices such as electrostatic precipitators, wet scrubbers, cyclones, or fabric filters.[24] Electrostatic precipitators and cyclones were widely utilized in older plants. The current trend, however, is to use an agglomerating device or cyclone followed by a fabric filter system. These collection systems are estimated to remove more than 99 percent of the carbon black from the combustion gases. Particulate emissions from carbon black plants are generally low for economic reasons and because of environmental control requirements.[23]

Combustion of hazardous waste is not believed to have any harmful effect on air pollution control devices. Wastes in one

TABLE 4.2-4. SIC CODES AND GEOGRAPHIC DISTRIBUTION OF INDUSTRIES GENERATING HAZARDOUS WASTE DESTRUCTIBLE IN THE OIL FURNACE CARBON BLACK PROCESS[19]

Category	SIC code of generating industry	Geographic location
F003	-	Widespread
K015	2865	Two plants (locations not known)
K023	2869	Richmond and El Sequendo, California; Kearney and Bridgeport, New Jersey; Baton Rouge, Louisiana; Bridgeville and Neville Island, Pennsylvania; Cicero and Millsdale, Illinois; Texas City, Texas
K093	2869	Texas, California, New Jersey

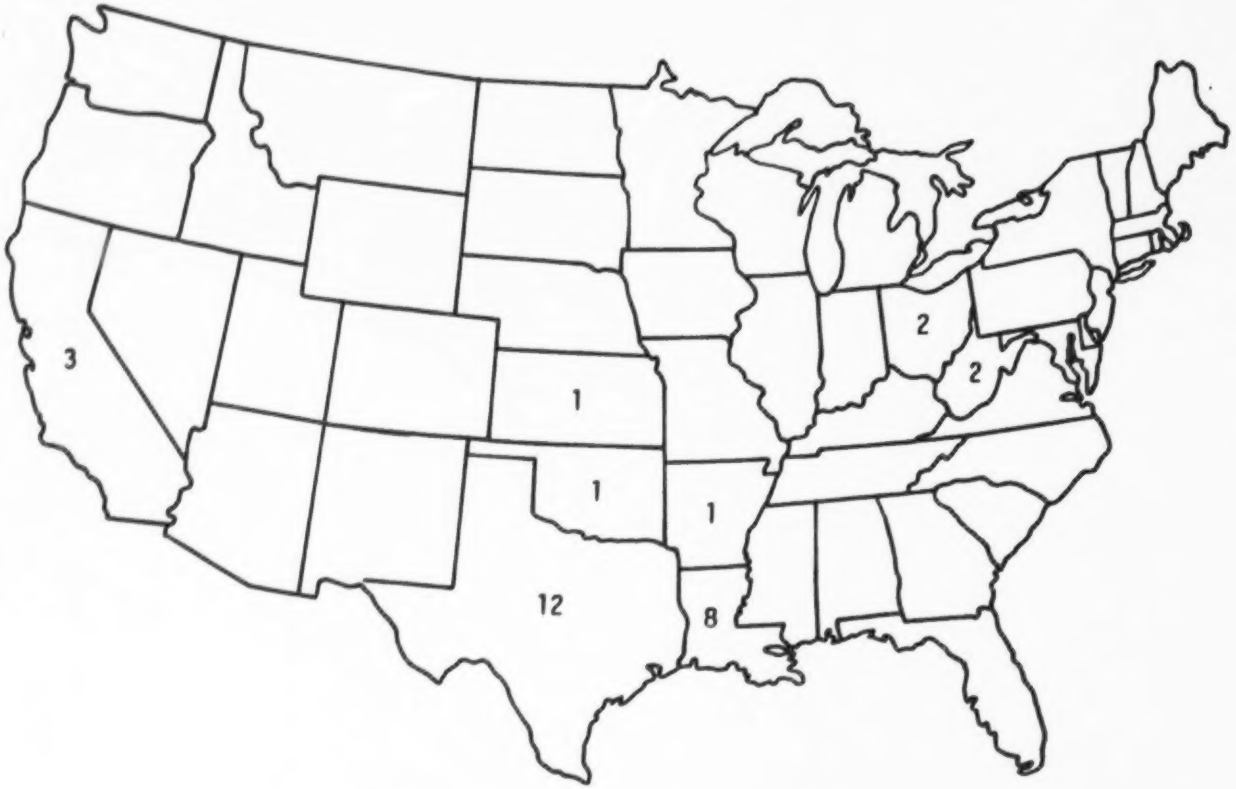

Figure 4.2-3. Geographic distribution of U.S. carbon black manufacturing plants.[23]

destructible waste category (K015), however, contain chlorinated aromatics, and a wet scrubber may be required to remove HCl (and Cl_2) in the off-gases. Most of the chlorine is believed to evolve as HCl because of the atmosphere of hydrogen in the furnace. Quantities of HCl emitted will vary greatly, depending on the amount of chlorine in the waste incinerated. The design of a scrubber system to control these emissions must consider the highly corrosive nature of chlorides on the materials of construction. A water treatment system for the scrubber effluent must also be included.

Environmental impact--Atmospheric emissions from carbon black furnace processes consist of CO, hydrogen sulfide, gaseous hydrocarbons (primarily acetylene), and particulates. At a number of plants, off-gas combustion (afterburner or CO boiler) is used to reduce these emissions. Any additional impact on these gaseous emissions due to hazardous waste combustion should be minimized by such off-gas combustion. Sulfide emissions are proportional to the level of sulfur in the feedstock; hence, H_2S and other sulfide compound emissions (CS_2, COS, etc.) will be low if the sulfur content of the waste and oil is low.

No major liquid process waste is generated by the furnace process because it is basically a gas-phase process. If a wet scrubber is used, however, a liquid effluent is produced. This effluent could be used in the pelletizer (see Figure 4.2-1), which would preclude the discharge of carbon black into wastewater.

The impact of hazardous waste combustion on solid waste produced from carbon black furnaces is believed to be negligible because insignificant quantities of solid waste are produced in such processes. Limited quantities of refractory material, scrap, and worn fabric filter bags are discarded and landfilled.

Fugitive emissions from carbon black production processes may result from maintenance procedures, leaks in plant conveying systems, or loading and unloading operations.[24] This may be a problem if hazardous compounds are adsorbed on the carbon black product before such compounds are completely destroyed. Most fugitive emissions can be reduced by a plantwide vacuum system ducted to a fabric filter and good housekeeping procedures which assure that all spillage is picked up and combusted or recycled. If such preventive measures are taken or if tests show that no significant hazardous components are adsorbed on the carbon black product, the combustion of hazardous wastes in the furnace should pose no significant problems.

4.2.2.4 Institutional Factors--

Because there is no generally acceptable substitute for carbon black in major applications, such as automobile tires, a steady growth of the domestic industry is expected.[23]

The carbon black industry (SIC 2895) is already considering the possibility of using waste tires as substitute feedstock to help alleviate the solid waste problem in the United States,[23] and it may not object to the combustion of hazardous waste in carbon black furnaces. It is a favorable factor that most of the 33 carbon black plants in the United States are located in rural areas far removed from large population centers.

Advances in technology and improved process economics kept carbon black prices stable from 1950 to 1973, but in recent years the cost of feedstock has increased more than fourfold, which has caused about a twofold increase in the price of large-volume rubber grades. This price increase could be controlled somewhat if hazardous wastes could be substituted for a portion of the conventional feedstock.

4.3 GLASS INDUSTRY

The glass industry consists of four major segments: glass containers, flat glass, pressed and blown glass, and fiberglass. The fiberglass segment (SIC-3296) is considered separately because its manufacturing process is vastly different from that for the other glass industry segments. The glass container segment (SIC-3221), which is the largest in terms of shipments and employees, accounts for approximately 57 percent of all glass melted, and the remaining glass production (except for fiberglass) is roughly divided between the flat glass (SIC-3211) and pressed and blown glass (SIC-3229) segments, which account for 24 and 19 percent, respectively.[25]

The three general types of container glass are amber, clear, and green. Green glass and clear glass are sometimes grouped together in a single category designated as "flint." Flint glass represented 85 percent of glass container production in 1976, and amber glass, 15 percent.[25] Glass container plants are located near the markets they serve. Figure 4.3-1 presents the geographic distribution of the major domestic glass container plants. As the figure shows, a large number of the plants are concentrated in the East, North Central, and Middle-Atlantic regions, which also are areas in which significant quantities of hazardous wastes are generated. Table 4.3-1, which gives a breakdown of the companies who own the 119 domestic plants, shows that five of these companies operate roughly half of these glass container plants.

Flat glass manufactured in the United States is converted into float, sheet, rolled, or plate glass. Float glass accounts for more than 90 percent of the total flat glass production.[25] As shown in Figure 4.3-2, most flat glass manufacturing plants are located in Pennsylvania, Ohio, Tennessee, Michigan, Illinois, Texas, and California.

The pressed and blown glass segment consists of approximately 155 manufacturing establishments (Table 4.3-2). Forty of these produce mostly hand-pressed and blown glass. Figure 4.3-3 which shows the locations of the plants, indicates that the majority are in New York, Pennsylvania, West Virginia, Ohio, Indiana, and Illinois.

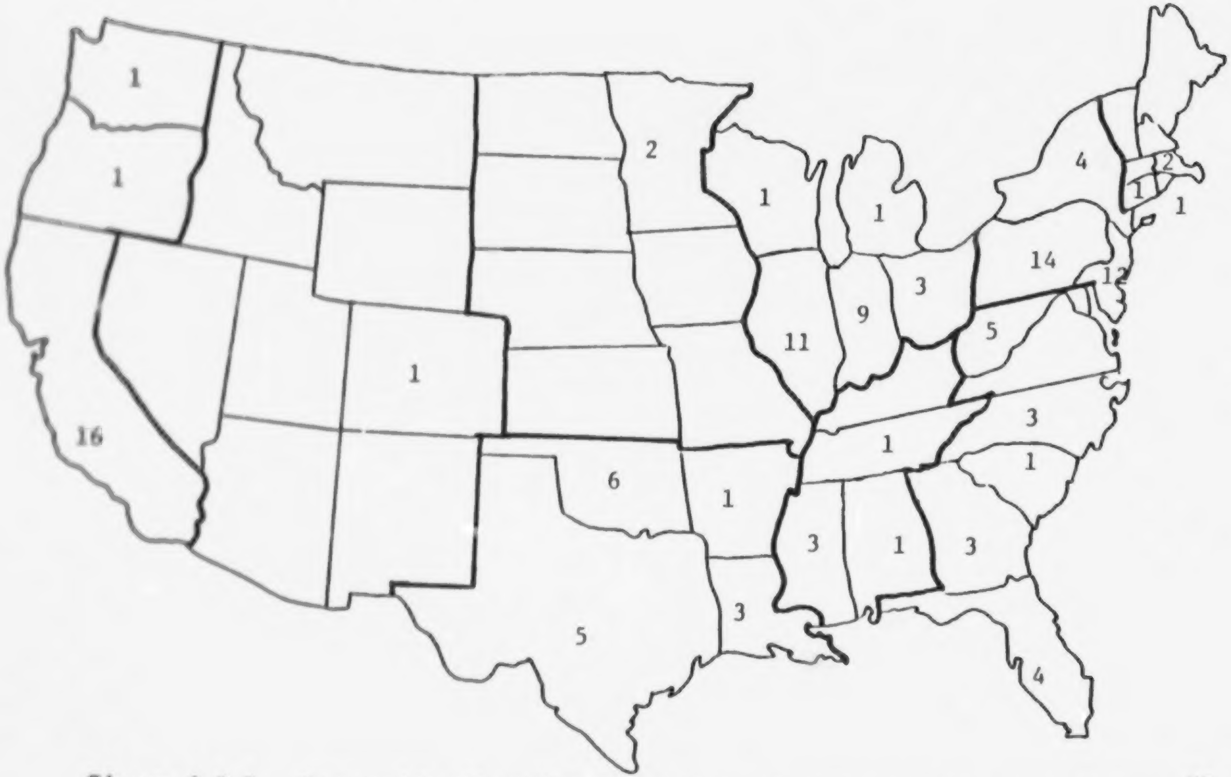
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Figure 4.3-1. Geographic distribution of U.S. glass container manufacturers.[25]

TABLE 4.3-1. MAJOR GLASS CONTAINER MANUFACTURERS IN THE UNITED STATES, 1975[25]

Manufacturer	No. of plants	Manufacturer	No. of plants
Anchor Hocking	9	Kerr Glass	7
Arkansas Glass	1	Latchford Glass	1
Ball Corporation	4	Leone Industries	2
Bartlett Collins	1	Liberty Glass	1
Brockway Glass	14	Madera Glass Co.	1
Chattanooga Glass	7	Metro Glass	4
Columbia Gas	1	Midland Glass	4
Diamond Glass	1	National Bottle Corp.	4
Gallo Glass	1	National Can	4
Glass Containers Corp.	12	Owens-Illinois	20
Glenshaw Glass	2	Thatcher Glass	6
Hillsboro Glass	1	Underwood Glass	1
Indian Head	7	Wheaton Glass	2
Industrial Glass	1	Total	119

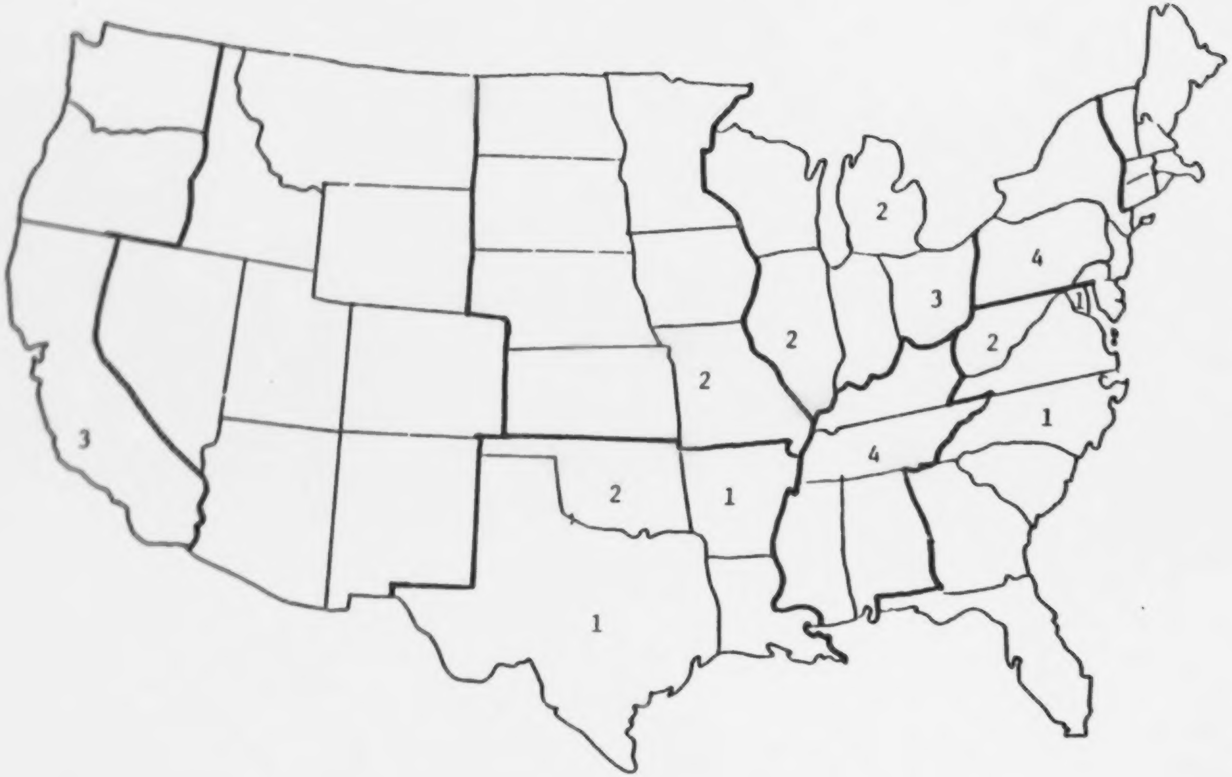
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Figure 4.3-2. Geographic distribution of U.S. flat glass manufacturers.[25]

TABLE 4.3-2. MAJOR PRESSED AND BLOWN GLASSWARE MANUFACTURERS IN THE UNITED STATES

Manufacturer	No. of plants	Manufacturer	No. of plants
American Optical	3	Kessler, Inc.	1
Anchor Hocking	4	King Seeley Thermos Company	2
Arrowhead Puritas	1	Labino Glass Laboratories	1
Atlantic Optical Moulding	1	Lancaster Glass Corporation	1
B and J Optical	1	Lenox Crystal	1
Bartlett-Collins	1	Lewis County Glass	1
Bausch and Lomb	1	Louie Glass Company	1
Beaumont Company	1	Marble King	1
Big Pin Glass Company	1	Masden Ind.	1
Blenko Glass Company	1	Mayflower Glass	1
Brock Glass Company	1	Mid-Atlantic	1
Brockway Glass	2	J. H. Millstein	1
E. O. Brody Company	1	Minners	1
Cambridge Glass	1	Multicolor Glass	1
Canton Glass	1	Nuclear-Pacific	1
Cataphote	1	Overmyer-Perram	1
Champion Agate Company	1	Owens-Illinois	10
Chemglass, Inc.	1	Pacific Glass Works	1
Corning Glass Works	14	Peltier Glass Company	1
Crescent Glass Company	1	Penbarthy Electromelt Intl., Inc.	1
Crystal Art Glass	1	Pennsboro Glass Company	1
Davis-Lynch Glass Company	1	Phoenix Glass Company	1
EMC Glass Corporation	1	Pikes Peak Glass Company	1
Eastman Kodak Company	1	Pilgrim Glass Corp.	1
Emerson and Cuming	1	Pittsburgh Corning Corp.	2
Elite Company, Inc.	1	Pape Scientific, Inc.	1
Erie Glass Mfg. Company	1	Potter Industry, Inc.	4
Erskine Glass and Manufacturing	1	RCA Corp.	1
Federal Glass Company	1	Rainbow Art Glass	1
Fenton Art Glass	1	Ray-Lite Glass, Inc.	1
Fischer and Porter Company	2	Reha Glass Company	1
Fostoria Art Glass	1	Rocky Mountain	1
Friedrich and Dimmock, Inc.	1	Rodifer Gleason Glass Corp.	1
GTE Sylvania, Inc.	4	St. Clair Glass Works	1
General Electric	9	Scandia Glass Works	1
Gentile Glass Company	1	Schott Optical Glass Company	1
Gillinder Brothers	1	Scott Depot Glass Company	1
Gladding-Vitro-Agate Company	1	Sellstrom Mfg.	1
Glass Works, Inc.	1	Earl Shelly Glass Company	1
Guernsey Glass Company	1	Sinclair Glass	1
Haley Glass Company	1	L. E. Smith Glass Company	1
Hamon Handcrafted Glass	1	Super Glass Corp.	1
Harvey Ind.	1	Swift Glass Corp.	1
Holophane	1	Techniglass, Inc.	1
Houze Glass Corp.	1	Thermal American Fused Quartz	1
Imperial Glass Corp.	1	Thomas Ind., Inc.	1
Indiana Glass Corp.	1	Variety Glass, Inc.	1
Industrial Glass and Plastics	1	Venejian Art Glass	1
Interpace Corp.	1	Victory Glass Company	1
Jeanette Corp.	1	Viking Glass Company	1
Jeanette Shade and Novelty Co.	1	West Virginia Glass Specialty Co.	1
Johnson Glass	1	Westinghouse Electric Corp.	1
Kanawa Glass Company	1	Westmoreland Glass Company	1
Kapp Glass, Inc.	1	Wheaton, Ind.	1
Kaufman Glass Company	1	The Paul Wissmach Co., Inc.	1

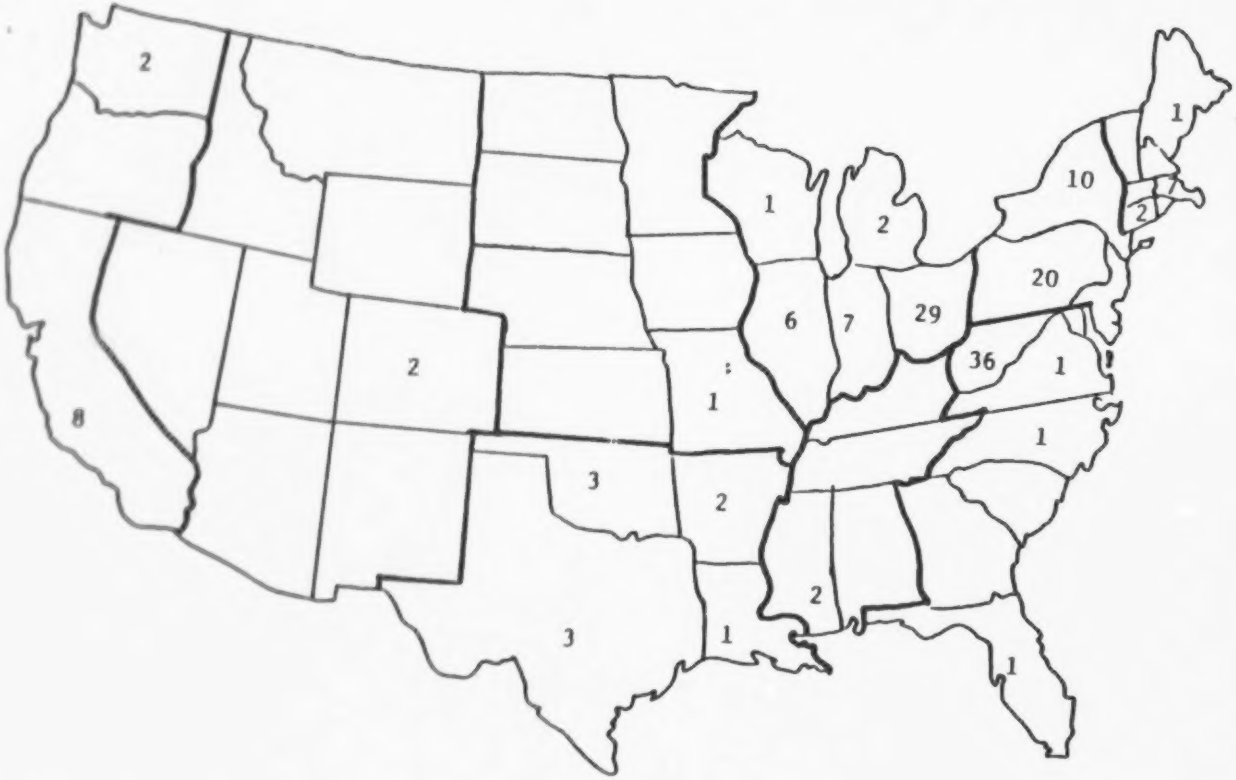
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Figure 4.3-3. Geographic distribution of U.S. pressed and blown glassware manufacturers.[25]

The various locations of fiberglass plants include Parkersburg, West Virginia, Fairburn, Georgia, Santa Clara, California, and Kansas City, Missouri. A listing of all fiberglass manufacturers and plant locations was not readily available.

4.3.1 Process Descriptions

The major processes in glass manufacturing are as follows:[25]

- Batch weighing and mixing
- Melting
- Forming
- Postforming
- Product packaging

In the flat glass industry segment, forming and postforming are usually integrated into one continuous process.

Figure 4.3-4 presents a typical process flow diagram for glass manufacture. Although drawn specifically for common soda-lime glasses, this figure has general application to most commercial glasses.

Basically, the manufacture of glass is the high-temperature conversion of raw materials into a homogeneous melt that can be fabricated into useful articles.[26] The major raw materials are glass sand (SiO_2), soda ash, limestone, and cullet (crushed waste glass). Minor ingredients include salt cake (Na_2SO_4), niter ($NaNO_3$), feldspar (Al_2O_3), arsenic, barium oxide, and boron oxide.[27] Mixing systems range from hand-operated to fully automated.

4.3.1.1 Melting Process--

The bulk of the soda-lime glass production is melted in direct-fired continuous, regenerative furnaces, which range in capacity from 45 to 272 Mg/day (50 to 300 tons/day) of glass.[28] Two kinds of furnaces are used: a side-port melter and an end-port melter. Figure 4.3-5 depicts a side-port melting furnace. This furnace consists of a dual chamber filled with brick checkerwork. While the products of combustion from the melter pass through and heat one chamber, combustion air is preheated in the

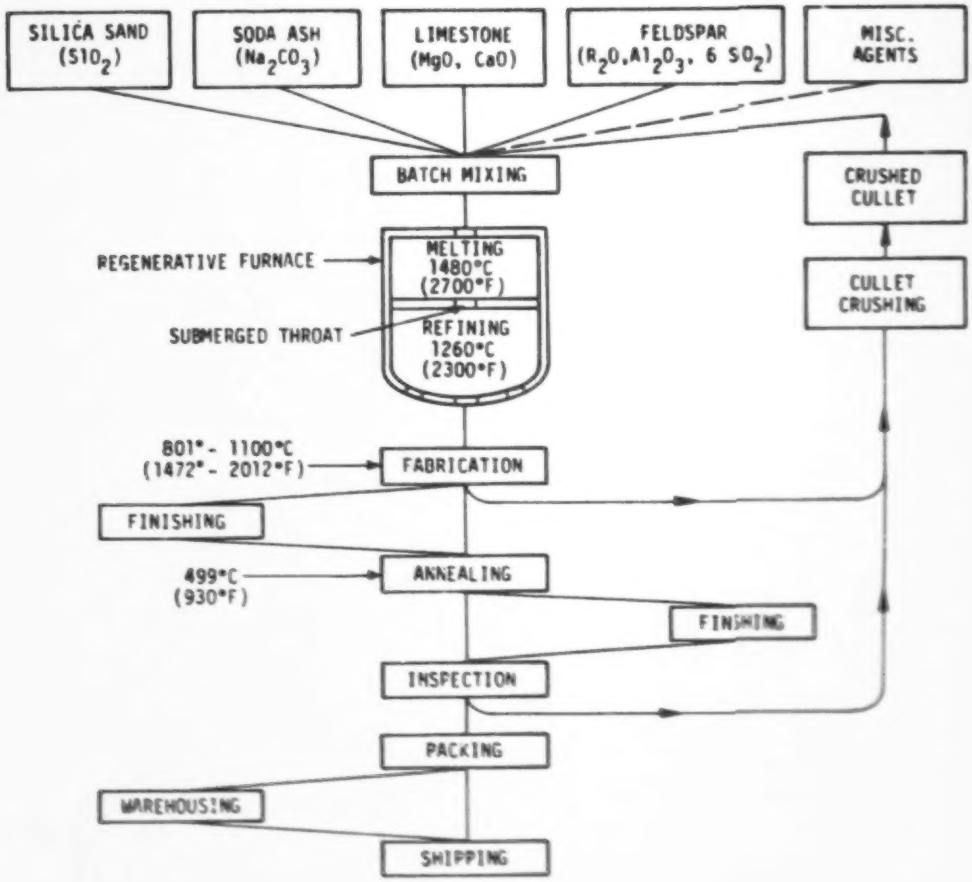
SILICA SAND (SiO2)
SODA ASH (Na2CO3)
LIMESTONE (MgO, CaO)
FELDSPAR (R2O.Al2O3, 6 SO2)
MISC. AGENTS
BATCH MIXING
CRUSHED CULLET
REGENERATIVE FURNACE
MELTING 1480°C (2700°F)
CULLET CRUSHING
SUBMERGED THROAT
REFINING 1260°C (2300°F)
801°- 1100°C (1472°- 2012°F)
FABRICATION
FINISHING
499°C (930°F)
ANNEALING
FINISHING
INSPECTION
PACKING
WAREHOUSING
SHIPPING

Figure 4.3-4. Flow diagram for soda-lime glass maufacture.[27]

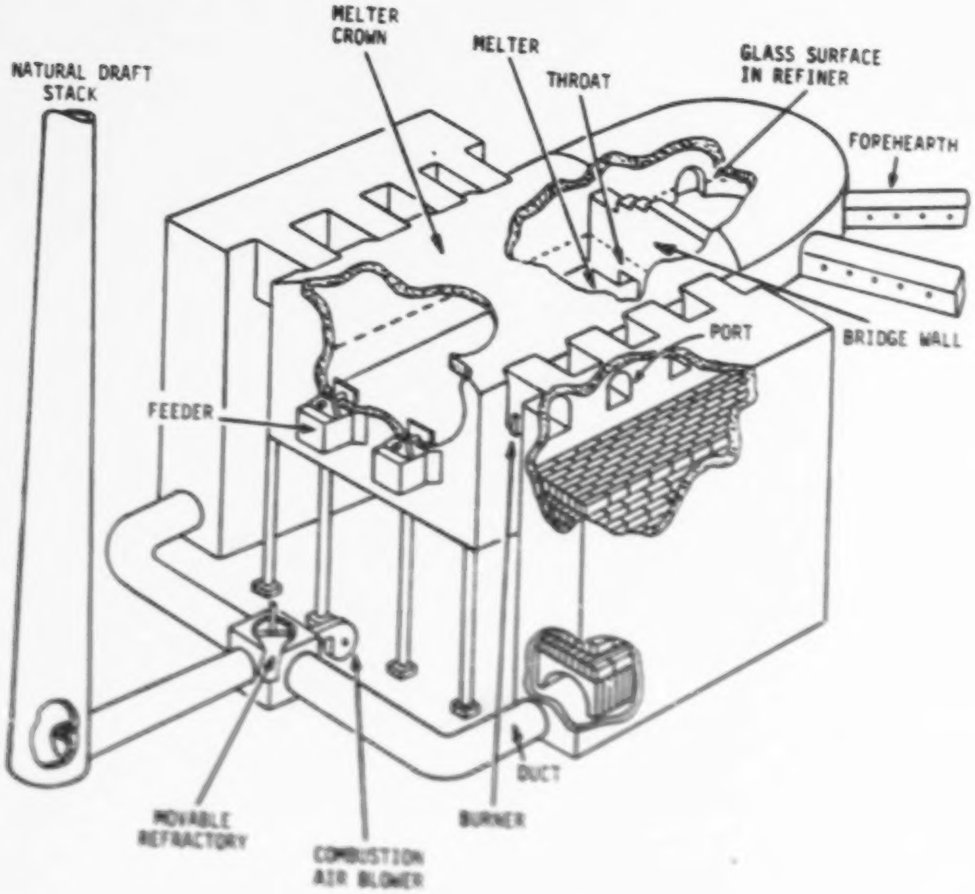
MELTER CROWN
NATURAL DRAFT STACK
MELTER
THROAT
GLASS SURFACE IN REFINER
FOREHEARTH
PORT
BRIDGE WALL
FEEDER
DUCT
MOVABLE REFRACTORY
COMBUSTION AIR BLOWER
BURNER

Figure 4.3-5. Regenerative side port glass-melting furnace.[27]

other chamber. The furnace is fired by gas or oil. The function of each chamber is interchanged by reversing the flow of air and combustion products every 15 to 20 minutes.[28] The batch-blended material is introduced into the furnace by screw- or reciprocating-type feeders. Dry material floats on top of the molten glass until it melts. As the carbonates decompose, they release carbon dioxide. Particles entrained in gas bubbles and other volatilized components of the feedstock are swept from the furnace by the hot gases passing across the molten surface. These materials are either deposited in the back checkerwork and refractory-lined passages or discharged into the atmosphere. In the refining section, the glass cools from 1480° (2700°) to about 1260°C (2300°F), and becomes viscous enough to form. It is then drawn from the furnace and sent to forming machines.

Table 4.3-3 shows typical emissions from glass melting furnaces. Generally, container glass melting furnaces have no pollution control equipment. Manufacturers usually rely on appropriate ingredient selection and good operating techniques to control emissions; however, many plants are now experimenting with such high-efficiency control devices as fabric filters and ESP's.[29] Pressed and blown glass furnaces, however, often use particulate control devices, predominantly ESP's.

TABLE 4.3-3. TYPICAL EMISSIONS FROM THE MANUFACTURE OF CONTAINER GLASS[27]

Emissions	Flint glass furnace	Amber glass furnace
Solids, g/Nm^3 (gr/scf)	0.071 (0.029)	0.101 (0.041)
Sulfur trioxide, ppm	17	15
Sulfur dioxide, ppm	250	315
Fluorine, ppm	2.2	1.9
Chlorine, ppm	4.9	4.1
Nitrogen oxides, ppm	340	640
Carbon monoxide, ppm	375	40

4.3.1.2 Forming Process--

Both glass containers and pressed and blown glass are formed in automated machines at temperatures of approximately 820° to

1090°C (1500° to 2000°F). This process uses various organic sprays and swabbing compounds to facilitate the release of the formed product from the hot metal mold.[25] Volatilization of these compounds results in emissions that exit through ventilators located in the roof of the building.

In flat glass manufacture, the forming process consists of allowing the molten glass to float onto a bath of molten tin and subsequently drawing it into a very large flat sheet.

4.3.1.3 Postforming Process--

The primary function in postforming is to remove detrimental, residual stresses by annealing. Natural gas is generally used as the fuel in the annealing step, and a temperature of about 930°F is attained. For glass containers and pressed and blown glass, decorative sprays and lubricity coatings are applied to the annealed product. Generally, a common ventilator is used for emissions from both forming and postforming processes.[25]

4.3.1.4 Fiberglass Manufacturing Process--

Both melting and forming operations in fiberglass manufacture differ from those in the other segments of the glass industry. The use of regenerative furnaces for production of fiberglass is declining, whereas the use of recuperative and electric furnaces is on the upswing. Melting temperatures in recuperators are in the range of 870° to 1090°C (1600° to 2000°F).[30] Figure 4.3-6 illustrates the operations involved in the production of fiberglass.

There are several types of fiberglass. Type E, the most common, has a composition similar to that shown for alumina-borosilicate glass. Because higher percentages of more volatile components are used, emissions from recuperative and regenerative fiberglass furnaces are much higher than those from container glass furnaces. Table 4.3-4, which lists typical emissions, shows that particulate loadings and fluoride levels are very high. The potential for hazardous pollutant emissions, such as

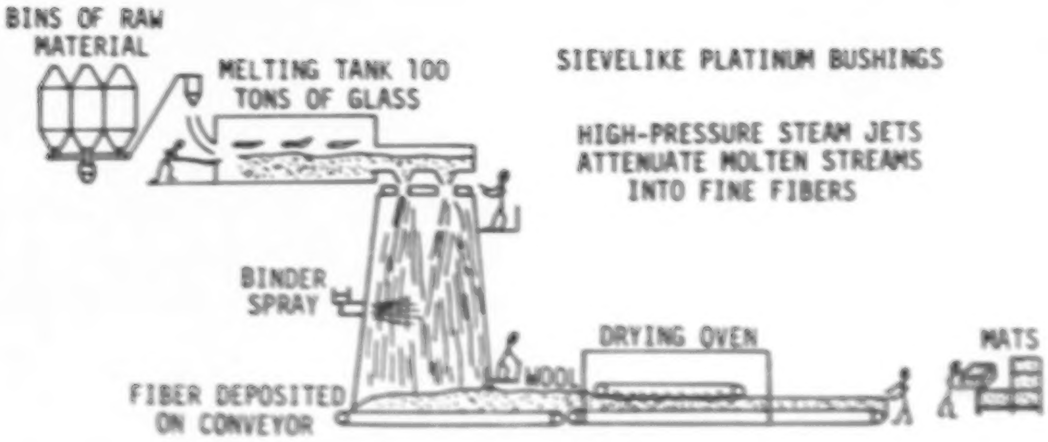
BINS OF RAW MATERIAL
MELTING TANK 100 TONS OF GLASS
SIEVELIKE PLATINUM BUSHINGS
HIGH-PRESSURE STEAM JETS ATTENUATE MOLTEN STREAMS INTO FINE FIBERS
BINDER SPRAY
DRYING OVEN
MATS
WOOL
FIBER DEPOSITED ON CONVEYOR

Figure 4.3-6. The operations in fiberglass production.[26]

compounds of beryllium, is greater in fiberglass manufacture than it is in container glass manufacture. Although fabric filters have been used to control emissions from fiberglass furnaces, they have met with only limited success. Electrostatic precipitators and wet scrubbers are also being used; however, the use of control measures is not an industrywide practice. The increased use of electric furnaces for fiberglass production is expected to reduce the generation of emissions considerably and thus preclude the need for control devices.

TABLE 4.3-4. TYPICAL EMISSIONS FROM RECUPERATIVE AND REGENERATIVE FIBERGLASS FURNACES[32]

Particulate loading	0.62 g/Nm^3 (0.25 gr/scf)
Gaseous fluoride	20-100 ppm
SO_x	40-80 ppm
B_2O_3	0.062 g/Nm^3 (0.025 gr/scf)
Opacity	30-80%

4.3.2 Process Assessment for Hazardous Waste Destruction

The large number of glass manufacturing plants and the high temperatures and moderate residence times achieved in the glass melting process make this industry attractive for thermal disposal of hazardous wastes.

The glass container segment, the largest in the industry, offers the greatest capacity for waste destruction. The pressed and blown glassware segment, which melts lower tonnages, also represents a viable alternative. In the flat glass industry, however, glass quality is a continuous problem,[31] and the introduction of extraneous materials, especially hazardous wastes, does not appear to be feasible. Although product quality is not a great concern in the fiberglass industry,[33] lower recuperator melting temperatures, high potential for hazardous emissions, and limited melting capacity present deterrents to consideration of fiberglass manufacturing processes for hazardous waste disposal.

In summary, the glass container and pressed and blown glassware segments of the glass industry appear to be good candidates for hazardous waste destruction. The preferred site of waste destruction would be in the melting furnaces, where the highest temperatures are attained. The following subsections address the melting processes of these two industry segments.

4.3.2.1 Technical Factors--

Compatibility of hazardous wastes with process fuel--Natural gas and oil are the primary fuels used. Producer gas is also used, but to a lesser extent. Propane and butane are also good for this application, but they are too expensive to be used much.[26] Natural gas is used more than oil because it is cleaner and because both the oil and its associated fuel systems are higher in cost. The Glass Packaging Institute indicated that fuel oil accounted for only 4 percent of fuel use at glass container plants in 1979 and 1980.[34] One major manufacturer of container and pressed and blown glass reported that fuel oil accounted for only 2 to 3 percent of their total fuel consumption in 1980.[35]

Liquid hazardous wastes would be more compatible with fuel oil than with natural gas because they could be blended with the oil and introduced into the melting furnace through the atomizing burners provided for firing oil. Because most furnaces are equipped with dual fuel capabilities, however, no compatibility problems should arise during the firing of natural gas.

Because both glass quality (primarily color) and emissions from glass furnaces are highly dependent on the composition of the metallic oxides that are charged to the furnace, it is important that the hazardous waste not contain any trace metals (e.g., nickel, iron, chromium, cobalt). One of the waste categories included in this study (K049) contains chromium (500 ppm) and lead (15 ppm); hence it would be eliminated from consideration.

Graphic determination of suitable waste categories--The dimensions of melting furnaces for the manufacture of container glass are similar to those of furnaces used for pressed and blown glass production. Outputs are as high as 270 Mg/day (300 tons/day). The maximum holding capacity of these furnaces is approximately 227 to 272 Mg (250 to 300 tons), corresponding with dimensions of 7.6 m x 15 m x 1.2 m (25 ft x 50 ft x 4 ft).[26] Typical flue gas volumetric flow rates are approximately 442 Nm^3/min (16,800 scfm).[27]

Pertinent process conditions for determining the time-temperature relationship in glass melting furnaces are shown below:

Volume of glass melting furnace:	140 m^3 (5000 ft^3)
Gas volumetric flow rate:	442 Nm^3/m (16,800 scfm)
Maximum reaction zone temperature:	1480°C (2700°F)
Exit gas temperature:[27]	616°C (1140°F)

Mean residence times (t) and fast-path residence times ($\bar{t}$) were computed for several temperatures between the maximum reaction zone temperature and the exit gas temperature. In Figure 4.3-7, the resulting process curves (plots of Δt and $\Delta\bar{t}$ versus T) are overlaid on the hazardous waste plots. Predictions regarding the potential of the melting process to destroy 99.99 percent of the hazardous wastes are shown in Table 4.3-5. It appears that wastes in 50 percent of the categories can be destroyed at the prevailing furnace temperatures.[30]

Effects on product quality and product application--The glass manufacturing industry has expressed a strong belief that hazardous wastes would be adequately destroyed at the temperatures and residence times attained in the melting furnaces.[33,34] The products of waste combustion would evolve in the flue gas, and no contamination of the glass product is expected as long as metallic constituents are not introduced in the charged wastes. Of the container glass types, product quality specifications are generally least demanding for amber glass.

Table 4.3-6 presents the major applications of pressed and blown glass. The nature of the end uses indicates that these

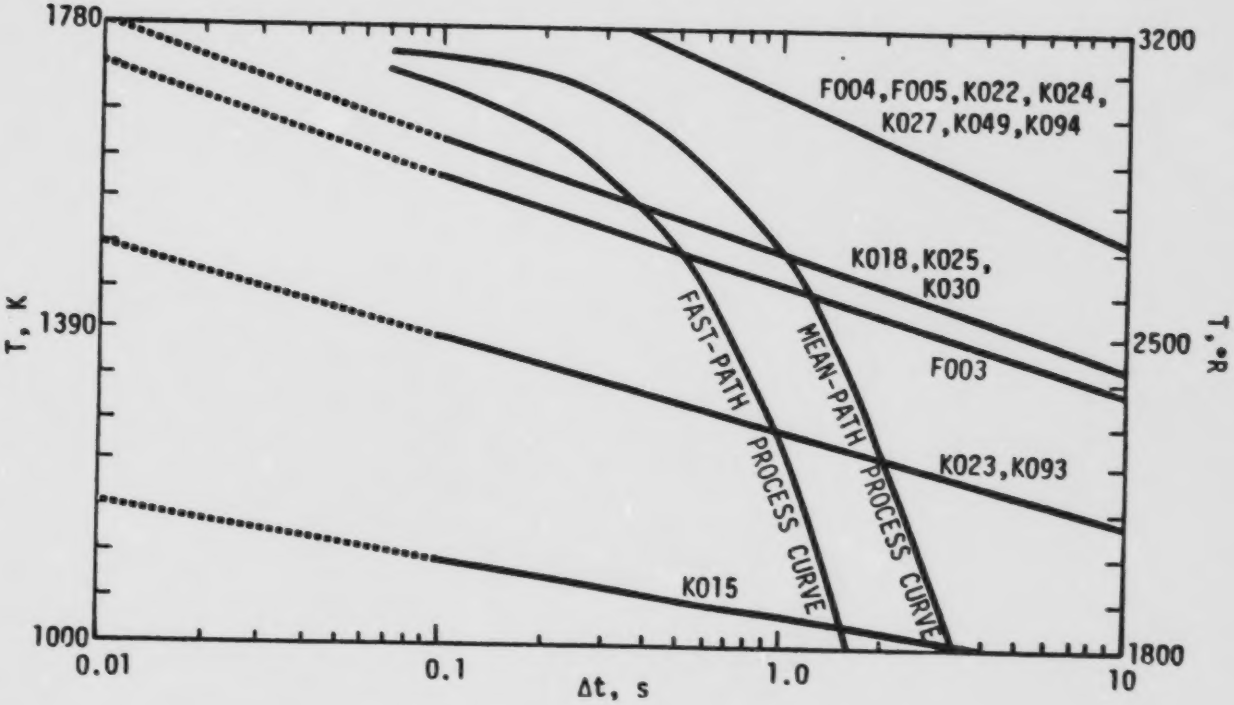

Figure 4.3-7. Hazardous waste destructibility predictions for melting furnaces in container glass and pressed and blown glass manufacture.

TABLE 4.3-5. FEASIBILITY OF GLASS MELTING PROCESS FOR THERMAL DESTRUCTION OF HAZARDOUS WASTES

Hazardous waste type													
F003	F004	F005	K015	K018	K022	K023	K024	K025	K027	K030	K049	K093	K094
Yes	No	No	Yes	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No

TABLE 4.3-6. PRODUCT APPLICATIONS FOR PRESSED AND BLOWN GLASS, SIC-3229[25]

Process and major products	SIC	Percent of industry shipment (value)	
		1972	1976
Table, kitchen, and art ware			
Machine-made	32291	33	39
Handmade		8	6
Lighting and electronic	32292	35	32
Scientific and industrial	32294	24	23
Total industry (percent)		100	100
(actual)		$1.1 billion	$1.6 billion

products must be absolutely free of hazardous waste contamination; the same is true for container glass.

Impact on process hardware--One of the primary problems in glass manufacture is that of obtaining a material suitable for the construction of glass-melting equipment. All materials are soluble in molten glass. When refractory corrosion could affect properties important to end use of the ware, platinum is used because it is almost insoluble in most glasses. No single refractory material, however, is suitable for all purposes in a glass tank. An ideal refractory should have (1) the ability to resist the action of heat without deformation, (2) a low rate of solution in the particular glass, (3) no source of chemical discoloration, (4) low thermal conductivity, and (5) high resistance to thermal stresses and spalling. Major types of refractories used in the glass industry include zircon, silica, fireclay, and high alumina.[26]

Glass industry personnel have expressed concern about the possibility of hot spots developing in the furnace if wastes are introduced in the melting furnaces.[31,33-35] The occurrence of this phenomenon could significantly reduce the life expectancy of the furnaces. Hot spots would also result in a drop in regenerator efficiency and a rise in fuel consumption.

Acceptable amounts of hazardous waste feed--For a melting furnace that processes 272 Mg/day (300 tons/day) of glass and has dimensions of 7.6 m x 15 m x 1.2 m (25 ft x 50 ft x 4 ft), typical natural gas (fuel) requirements are about 200 m^3/Mg (6500 ft^3/ton) of glass.[28]

Assuming a caloric value of 3.7 MJ/m^3 (1000 Btu/ft^3) for natural gas,[26] heat input to the furnace through the fuel is 7.6 MJ/kg (6.5 x 10^6 Btu/ton) of glass produced.

The average heating value of the seven waste categories previously shown to be destructible is 19.8 MJ/kg (8500 Btu/lb). Based on the postulation that the hazardous wastes would account for 10 percent of the heat input to the furnace, the amount of hazardous waste feed would be:

$$\frac{0.1 \times 7.6\ \text{MJ}}{\text{kg of glass}} \times \frac{1\ \text{kg waste}}{19.8\ \text{MJ input}} = 38.2\ \frac{\text{kg waste}}{\text{Mg glass}}$$

For a glass production rate of 272 Mg/day (300 tons/day), and an assumed process operation of 260 days/year, the hazardous waste disposal rate would be:

$$\frac{38.2\ \text{kg}}{\text{Mg glass}} \times \frac{272\ \text{Mg glass}}{\text{day}} \times \frac{260\ \text{days}}{\text{yr}} \times \frac{1\ \text{Mg}}{1000\ \text{kg}}$$

$$= 2700\ \text{Mg/yr}$$

Provisions for waste introduction--In those furnaces where fuel oil is the primary fuel, the hazardous wastes could be blended with the oil and the mixture could be preheated before being fed into atomizing burners. Blending of fuel and waste, however, is not feasible for natural gas-fired furnaces; therefore, additional burner ports might have to be installed to introduce the wastes. The locations of these burners should be such that the flame characteristics are not significantly affected.

Projected trends in process fuel--Table 4.3-7 presents a breakdown of the consumption of various types of fuel in glass container production. It should be noted that the reported consumption figures include operations other than glass melting, (e.g., space heating, glazing, and annealing); however, these other operations do not use fuel oil. Although natural gas is clearly the predominant fuel, the use of fuel oil appears to be increasing in recent years.[25]

4.3.2.2 Geographic Matching of Industry Locations and Waste Generators--

Table 4.3-8 presents the geographic distribution of the waste categories that conceivably could be destroyed in a glass melting furnace. Figures 4.3-1 and 4.3-3 (presented earlier) show that the majority of the glass container and pressed and blown glass plants are concentrated in the eastern United States, particularly New York, New Jersey, and Pennsylvania. Because the

TABLE 4.3-7. BREAKDOWN OF FUEL CONSUMPTION FOR CONTAINER GLASS MANUFACTURE, 1978[36]

Oil	590 Ml (155 x 10^6 gal)
Residual	320 Ml (84 x 10^6 gal)
Distillate	270 Ml (71 x 10^6 gal)
Natural gas	2.9 Gm^3 (103 x 10^9 ft^3)
LPG	15 Gg (33 x 10^6 lb)
Energy consumption (all fuels)	1.4 x 10^8 GJ (131 x 10^{12} Btu)
Electrical energy consumption	4872 x 10^6 kWh
Total energy consumption (fuels and electrical energy)	1.6 x 10^8 GJ (148 x 10^{12} Btu)

TABLE 4.3-8. SIC CODES AND GEOGRAPHIC DISTRIBUTION OF INDUSTRIES GENERATING HAZARDOUS WASTE DESTRUCTIBLE IN GLASS MANUFACTURING FURNACES[19]

Hazardous waste type	SIC code for waste generating industry	Geographic distribution of waste
F003	-	Widespread
K015	2865	Two plants (locations not known)
K018	2869	Houston and Freeport, Texas; Lake Charles and Baton Rouge, Louisiana; Deepwater, New Jersey; Long Beach, California
K023	2869	Richmond and El Sequendo, California; Kearney and Bridgeport, New Jersey; Baton Rouge, Louisiana; Bridgeville and Neville Island, Pennsylvania; Cicero and Millsdale, Illinois; Texas City, Texas
K025	2865	Bound Brook, New Jersey; Willow Island, West Virginia; Beaumont, Texas; Gibbstown, New Jersey; Geismar, Louisiana; New Martinville, West Virginia
K030	2869	Freeport, Deer Park, and Corpus Christi, Texas; Baton Rouge, Lake Charles, and Plaquemine, Louisiana; Pittsburg, California; Louisville, Kentucky; Wichita, Kansas
K093	2869	Texas, California, New Jersey

State of New Jersey is also a generator of four of the destructible waste categories (K018, K023, K025, K093), there is very good matching between waste generator and glass industry locations for these wastes. Waste K023 is generated in Pennsylvania and K025, in West Virginia, where many glass plants (especially pressed and blown glass) are located. Most of the destructible wastes are also generated in California, where a total of 24 container glass and pressed and blown glass plants are situated. Significant quantities of the destructible wastes are also generated in Texas and Louisiana, but few glass plants are located in these states.

4.3.2.3 Environmental Factors--

Impact on air pollution control devices--Control technology for glass furnaces is in a developmental state. The ESP appears to be emerging as the preferred control device.[25] Only a few control device installations are in continuous operation. Two tableware glass plants operated by Owens-Illinois, one in California and the other in Illinois, use a fabric filter and an ESP, respectively, for controlling particulates from their glass furnaces; an Anchor Hocking four-furnace tableware plant in Ohio has been using ESP's for this purpose since 1977. Combustion of hazardous wastes in the furnace is not expected to have any harmful effect on such air pollution control devices.

High carbon monoxide emissions (375 ppm) have been measured in flint glass furnaces.[27] The potential for increased CO levels and hydrocarbon emissions exists during the destruction of hazardous wastes, and an afterburner may be necessary to control such emissions. The only known afterburner installation is at an Owens-Corning fiberglass plant in Fairburn, Georgia. Adequate combustion control can also be exercised to control CO and HC levels.

Chlorine and fluorine levels in the exhaust from container glass furnaces are about 2 to 4 ppm (see Table 4.3-3).[27] Destructible waste types K015, K018, and K030 contain halogenated compounds, which could cause an increase in halogen emissions.

Test burns definitely should be conducted to determine the nature of emissions resulting from the combustion of hazardous wastes in glass melting furnaces. The results of such tests would dictate whether additional air pollution control equipment is required.

Environmental impact--In glass manufacture, the melting process is the major source of emissions. The volume of emissions varies from furnace to furnace and depends on the composition of the glass being produced. To a lesser degree, the volume also depends on the design and operating characteristics of the furnace and the type of fuel used. Flint glass has the lowest emission rate. Container glass furnaces can usually meet both process weight regulations and 40 percent opacity limitations without controls, but they have difficulty staying consistently below the 10 percent opacity limitations imposed by some agencies. The atmospheric impact will have to be closely monitored when charging hazardous wastes into the melting furnace.

Minor quantities of liquid/solid wastes are generated in the glass industry. These include cullet quench water, mold degreasing waste, and waste lubricants. Hazardous waste combustion should have no impact on the generation of these wastes.

4.3.2.4 Institutional Factors--

Historically, the growth of the glass container industry has fluctuated considerably, but shipments have steadily increased at an average annual rate of 6 percent since 1967. A large proportion of this growth is attributable to the popularity of the nonreturnable beverage bottle. The growth in shipments has slowed down in recent years, and future growth may be tied to legislation restricting the use of nonreturnable containers.[25] Production levels in 1980 were about 20 percent higher than 1974 levels.

Future growth trends are somewhat difficult to estimate for the pressed and blown glass segment. The diversity of this sector tends to exempt it from the fluctuations experienced by other glass industry segments. An annual growth rate of 5 to 8 percent appears reasonable for this segment.[25]

The concept of burning wastes in glass melting furnaces is not entirely new to the glass industry. The Glass Packaging Institute indicated that a glass container plant operated by Glass Containers Corporation has used the glass melting process to destroy hazardous components in waste lubricating oils generated at the plant.[34] These waste oils, which contained about 1 percent trichloroethylene, were initially centrifuged to remove sludges and metallic components before being charged to the furnace. No problems were encountered with the burning, nor was product (glass) quality affected. In spite of this positive experience, glass manufacturers still appear to be somewhat reluctant to accept the idea of charging hazardous wastes in their melting furnaces.[31,35]

Customers also may not readily welcome the idea of introducing hazardous wastes in glass melting furnaces, especially when the glass products are used for storing or processing food materials. The presence of most glass plants in highly populated areas is another unfavorable factor.

4.4 IRON AND STEEL INDUSTRY

Figure 4.4-1 presents a general material flow diagram for the iron and steel industry. The following high-temperature processes were considered for the feasibility of thermal destruction of hazardous wastes at high temperatures.

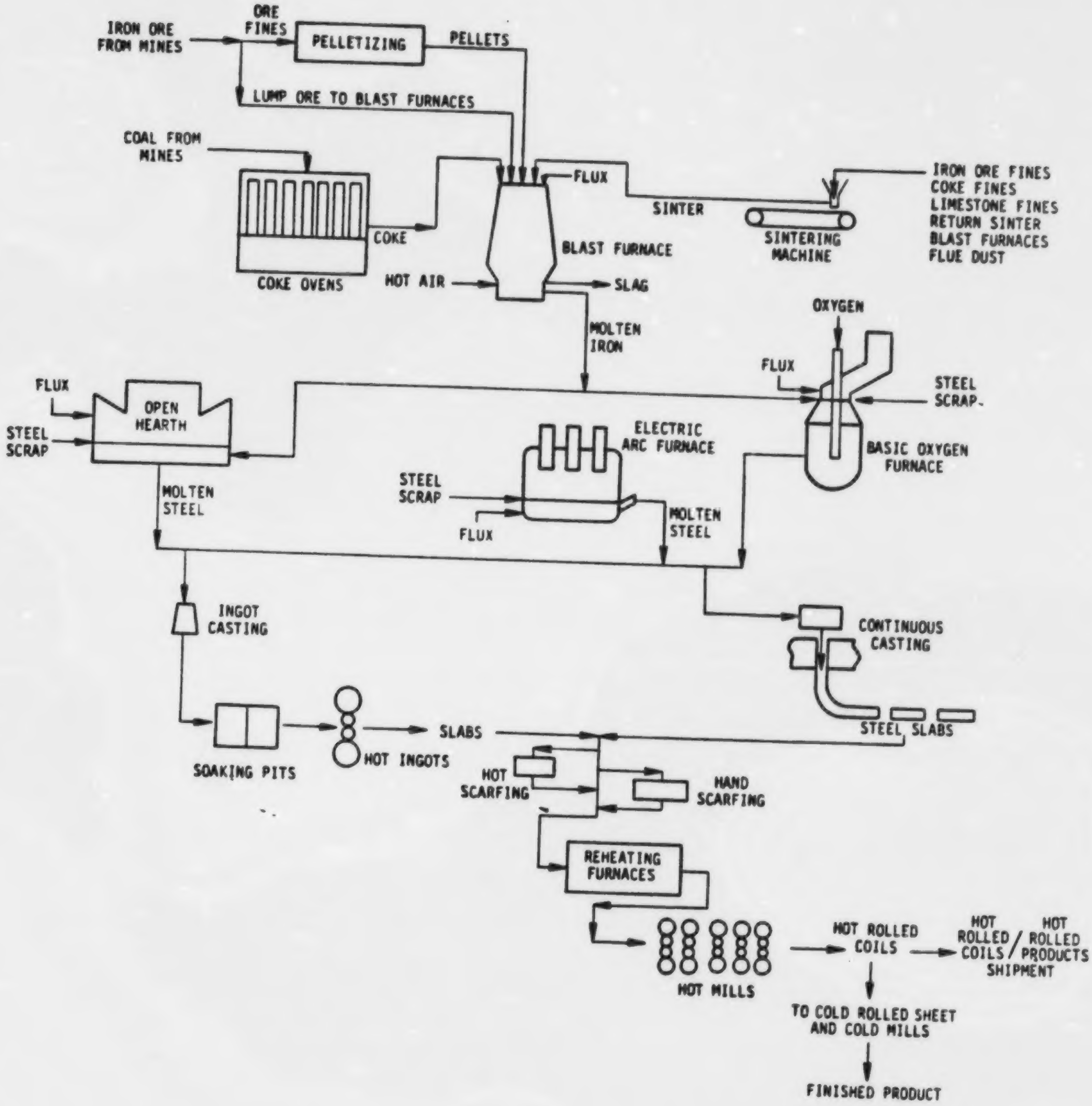
IRON ORE FROM MINES
ORE FINES
PELLETIZING
PELLETS
LUMP ORE TO BLAST FURNACES
COAL FROM MINES
COKE OVENS
COKE
FLUX
SINTER
IRON ORE FINES
COKE FINES
LIMESTONE FINES
RETURN SINTER
BLAST FURNACES
FLUE DUST
SINTERING MACHINE
BLAST FURNACE
HOT AIR
SLAG
MOLTEN IRON
OXYGEN
FLUX
STEEL SCRAP
FLUX
STEEL SCRAP
OPEN HEARTH
ELECTRIC ARC FURNACE
BASIC OXYGEN FURNACE
STEEL SCRAP
FLUX
MOLTEN STEEL
MOLTEN STEEL
INGOT CASTING
CONTINUOUS CASTING
STEEL SLABS
SOAKING PITS
HOT INGOTS
SLABS
HOT SCARFING
HAND SCARFING
REHEATING FURNACES
HOT MILLS
HOT ROLLED COILS
HOT ROLLED COILS / HOT ROLLED PRODUCTS SHIPMENT
TO COLD ROLLED SHEET AND COLD MILLS
FINISHED PRODUCT

Figure 4.4-1. General material flow diagram for iron and steel industry.

Process	Temperature range °C	Temperature range °F
Coke ovens	1260-1330	(2300-2400)
Sinter plants	1290-1450	(2350-2600)
Pelletizing plants	1220-1370	(2200-2500)
Basic oxygen furnaces (BOF)	1650-1820	(3000-3300)
Electric arc furnaces (EAF)	1570-1650	(2850-3000)
Soaking pits	1180-1340	(2150-2450)
Blast furnaces (BF)	1110-1870	(2000-3400)
Open hearths (OH)	1610-1650	(2900-3000)

Each process was examined with respect to the following issues:

- Suitability of time/temperature profiles to achieve 99.99 percent destruction of certain waste categories.
- Hazardous waste handling, charging limitations, and safety considerations.
- Handling of the incinerated products and other possible environmental impacts.
- Impact on the refractory lining of the furnaces.
- Effects of hazardous waste incineration on product quality.

4.4.1 Process Description

Each of the processes not considered feasible is briefly discussed first. The feasible processes are then discussed in more detail.

4.4.1.1 Coke Ovens--

Nearly all metallurgical coke, which is the major fuel used in blast furnaces, is made by the byproduct oven process. In this process, coal is heated in the absence of air, which drives off most of the volatile matter, part of the sulfur, and the contained moisture. The outgoing gases from this process are collected as byproduct gas. The residue is about 90 percent carbon, and the remainder is ash and sulfur. After it is screened, this metallurgical coke is sent to the blast furnace.

In the coke-making process, finely ground metallurgical coal is charged into a coke rectangular oven. Older ovens may be from 9 to 12 meters (30 to 40 feet) long, 1.8 to 4.3 meters (6 to 14 feet) high, and 0.28 to 0.56 meter (11 to 22 inches) wide. More recent ovens are 17 meters (55 feet) long, 4 to 6 meters (13 to 20 feet) high, and about 0.46 meter (18 inches) wide. Groups of these ovens are called batteries. As many as 70 to 100 ovens may be grouped together in a battery to facilitate the charging of the coal into the ovens and the pushing out of the coke produced when the coking process is complete. The coal is charged through three or four charging holes situated in a row on top of each oven. Specially designed hopper cars (known as larry cars) discharge coal from the bottom into the charging holes. The coal is carbonized in a reducing atmosphere for a period of 15 to 18 hours. The ovens are heated indirectly by burning cleaned coke oven gas in the combustion chambers on both sides of the oven. Combustion air is preheated by passing it through a regenerative brick matrix (known as checkerwork) which is located under the battery.

The gases released during carbonization are ducted to the byproduct plant, where useful byproducts such as tar, ammonia, and light oil are recovered from the gas. The removal process in the byproducts plant also cleans the gas, which still has heating value. This cleaned gas is used for combustion in the coke ovens and in other fuel burning units in the steel plant.

The temperature attained in the oven during carbonization of furnace coke is about 1300°C (2400°F). The carbonization temperatures in manufacturing foundry coke are lower, and the coking time varies from 24 to 32 hours. When the coke is ready, the doors on both sides of the oven are removed, and a ram mounted on a pusher machine pushes the hot coke into a receiving quench car. The quench car takes the coke to a quench tower where it is cooled with water sprays.

Considerable fugitive emissions can be generated in the coke-making process. Fugitive emissions occur during charging (from the charging holes and the larry car hoppers); during carbonization (from the doors, charging hole lids, and offtake pipes); and during the pushing of coke. These fugitive emissions are difficult to control. This emission potential and the lack of any feasible method for introducing hazardous wastes make it impossible to use today's coke oven process for waste pyrolysis.

Although cofiring of liquid hazardous wastes in the coke oven combustion chamber is conceptually possible, it is not considered technically feasible. The majority of coke ovens fire recycled coke oven gas in a complex heating system that uses multiple burners in each flue; temperature control is critical. Cofiring would require major retrofitting. Because any unincinerated products would be vented directly to the atmosphere through the stack, which generally does not have any air pollution control equipment, coke ovens were eliminated from further consideration.

4.4.1.2 Sinter Plant--

Sintering plants convert iron-ore fines, limestone fines, recycled metallurgical dusts, and mill scale (oily metal wastes from finishing operations) into an agglomerated product for charging into the blast furnace. The iron-bearing materials are mixed with coke breeze (coke not suitable for blast furnace feed) and then deposited in a layer on a slow moving grate. The combustion is initiated by igniting the surface of the bed by use of a gas or oil-fired ignition box at the head end of the machine. An induced draft applied at the bottom of the bed moves a narrow, high-temperature burning zone through the bed. Within this narrow fusion zone, the surfaces of adjacent particles reach fusion temperature and the gangue constituents form a semiliquid slag. Bonding is effected by a combination of fusion, grain growth, and liquid formation. Air pulled through the bed from the top quenches the rear edge of the advancing fusion zone as it moves downwards through the bed. The final product consists of a cellular mass of ore bonded in a slag matrix. The sintered material is cooled, crushed, and screened to remove the undersize, which is recycled.

Sintering machines process a wide variety of feed materials, and the raw material handling systems generally consist of open bins and conveyors. Also, fusion is incomplete in this process and does not necessarily encompass the entire mass. Because retention times are short, any hazardous waste added to the sinter feed might not be completely incinerated.

The maximum temperatures attained in the sinter bed are 1290° to 1430°C (2350° to 2600°F), but these temperatures are achieved only in the narrow fusion zone; thus, the residence time at these high temperatures is inherently short. By the time the draft air passes through the 25 to 30 cm (10 to 12 inches) of bed, the temperature falls below 650°C (1200°F). This means unincinerated or partly incinerated hazardous wastes could escape through the gas collection system and into the atmosphere. Cofiring wastes in the ignition hood is not feasible because of the short retention time, the relatively small fuel consumption 109 MJ/Mg sinter (about 160,000 Btu/ton), and the open structure of the hood, which could allow combustion products to escape into the workplace. These factors make sinter plants unsuitable for hazardous waste destruction.

4.4.1.3 Pelletizing--

Low-grade iron ores are subjected to various ore-treatment processes to increase their iron content. The ore fines obtained after crushing and froth flotation are agglomerated into pellets. The main advantages of pelletizing are achievement of controlled chemical analysis by mixing desired materials in the pellet mix, resistance to weathering and freezing, relative size uniformity, physical strength, and good reducibility. The concentrates are usually formed into balls (pellets) ranging in size from 1.0 to

1.3 cm (3/8 to 1/2 inch) in a balling mill, and the green pellets are then fired in kilns. In rotary kiln and grate kiln furnaces, essentially all the heat to the system is supplied countercurrently to the feed by a burner at the discharge end of the kiln. The hot gases from the kiln pass over and through the grate and supply the heat necessary to dry and pre-fire the pellets. Auxiliary burners are sometimes used near the grate to develop adequate strength in the pellets to withstand the fall into the kiln. The maximum temperature attained in the kiln is 1400°C (2500°F). The fuel requirements for induration (heat treatment of pellets) is estimated to be about 730 MJ/Mg (625,000 Btu per ton) for magnetite and about 860 MJ/Mg (893,000 Btu per ton) for hematite.[37]

The potential exists for incinerating selected hazardous wastes in the rotary kiln by cofiring the liquid wastes with the fuel when time and temperature conditions are suitable. Almost all the pelletizing plants that have kilns, however, are in the State of Minnesota, close to the iron ore mines (four plants). These plants generally are in inaccessible areas, far from the hazardous waste generators. Even though it is possible to incinerate hazardous wastes in these kilns, the logistics of transportation and the limited number of kilns preclude pelletizing kilns as a viable option for hazardous waste incineration.

4.4.1.4 Basic Oxygen Furnace--

In this process, a water-cooled lance is used to blow pure oxygen into the molten iron in the BOF vessel. The oxygen reacts with the carbon contained in the iron to supply the process heat. A temperature of 1670°C (3000°F) is developed in the body of the vessel, and temperatures at the lance tip reach 2220° to 2500°C (4000° to 4500°F). Ordinarily, no external fuel is used. The reaction product gases exit through a hood to gas-cleaning equipment. During the oxygen blow, the gases contain about 90 percent CO and 10 percent CO_2. In the case of open-hood designs, excess air enters the annulus between the hood and the mouth of the vessel and the CO is burned to CO_2, which generates temperatures in excess of 2800°C (5000°F). The gases are cooled by direct water sprays and cleaned by electrostatic precipitators. In the case of closed-hood systems, the CO combustion is suppressed by the close fit between the hood and the vessel, which minimizes air infiltration. The CO-rich exhaust gases pass through a quencher for cooling and then to venturi scrubbers. These exhaust gases can be stored for use as a fuel or flared and exhausted to the atmosphere.

Steel scrap is charged into the BOF vessel by tilting the vessel forward and charging the scrap directly into the vessel. After the scrap is charged, the hot metal is charged by tilting the vessel forward while metal is poured into the vessel from a transfer ladle by means of an overhead crane. After the hot metal is charged, the vessel is brought into an upright position, and the oxygen lance is introduced from the top. Fugitive emissions occur during the charging operations and, generally, any time the vessel is tilted away from the primary collection hood. Newer shops have secondary capture systems for control of these emissions. Given the high temperatures, relatively long gas retention time, and the pollution control devices used, this process has potential for hazardous wastes incineration, in spite of the potential for fugitive emissions from the open-hood systems.

Charging hazardous waste into the BOF vessel, however, could be potentially dangerous and time-consuming. Wastes would have to be segregated and charged separately, which would involve additional vessel tilting and an additional materials-handling step. The segregation and drying of wastes would also require additional space, which may not be available in an operating BOF shop. Also, the charging of uncombined water and organic wastes into the BOF vessel could pose an explosion hazard. The productivity of the BOF process is high because the average tap-to-tap time (time from charging the iron until removal of the steel) is typically less than one hour. A regular supply of wastes to meet the charging schedule could impose delays, particularly in light of the strict precautions necessary to handle these wastes. Such constraints would slow down the steelmaking process on these high-volume production units, which would probably not be acceptable to the steel industry.

In some BOF shops, scrap is preheated to reduce the hot metal requirement. This is accomplished by charging extra scrap and then heating the scrap by means of natural gas or oil and oxygen introduced through an auxiliary lance. Depending on the amount of scrap charged, the preheating lasts 10 to 20 minutes. This is one potential practice where hazardous wastes might be used. The use of wastes in this procedure should not unduly affect the quality of steel, as the incineration of wastes would be completed during the scrap preheating period. Unfortunately, the number of BOF shops with open-hood configuration, where scrap preheating coupled with waste incineration could be practiced, is limited. Only 9 of the 36 BOF shops in the United States have an open-hood configuration, and not all of them practice scrap-preheating. Those that do, only practice it periodically. Because of these constraints, this method of waste disposal is not considered a viable option.

4.4.1.5 Electric Arc Furnaces--

Electric arc furnaces are refractory-lined cylindrical basins. Electrical energy is supplied through large graphite electrodes extending down through the roof of the furnace. The charge consists of select steel scrap, cast iron scrap, pig iron, alloying elements, and flux to achieve the desired composition. Melting is accomplished by the heat of the arc between the graphite electrodes and the charge. Scrap is charged by raising the electrodes and swinging the roof and electrodes to one side. This method of charging generates heavy emissions, which generally are controlled by direct-shell evacuation, canopy hoods, or enclosed buildings evacuated to a fabric filter. Complete capture of the emissions is not achieved.

Because of the high degree of furnace atmosphere control (oxidizing or reducing) that can be achieved, low-carbon, high-carbon, and alloy steels are all made in electric furnaces. This is a batch operation with tap-to-tap (time from materials charge to steel removal) times of 2 to 8 hours, depending on the quality of steel and the use of oxygen. Temperatures range from 1570° to 1650°C (2850° to 3000°F). The capacities of electric arc furnaces range widely, from 4.5 to 320 Mg (5 to 350 tons) per heat (one production cycle), depending on the quality of the steels made and the desired finished products.

These high-efficiency furnaces could not accommodate the charging of large quantities of hazardous wastes without disruption to production. The electric furnace is not considered a viable option for hazardous waste incineration for several reasons: the fugitive emissions that escape during charging, emissions that escape through electrode holes during meltdown, fugitive emissions generated by oxygen lancing, emissions generated by slagging and tapping, and finally, the logistic and safety problems involved in the handling and charging of hazardous wastes.

4.4.1.6 Soaking Pits--

Steel ingots are cast in molds at the melting shop and allowed to solidify until a sufficiently thick skin is formed to contain the molten interior. The molds are then stripped from the ingots by means of a specially designed crane. The hot ingots are transferred to the soaking pits before they are rolled into slabs. The purpose of the soaking pits is to heat the ingots to the desired rolling temperature and to achieve a uniform temperature of 1150° to 1330°C (2100° to 2400°F) throughout. The soaking pits are rectangular boxes with removable covers.

The pit cover is opened, and 6 to 10 ingots (depending on the size of the pit) are charged by crane. After the cover is replaced, the pit is fired by burners in the end walls. The fuels are natural gas, coke oven gas, and oil. The exit gases pass through openings in the lower part of the pit, and proceed through recuperators to a stack. Each batch is heated for 4 to 12 hours, depending on the elapsed time between stripping and charging. Theoretically, it is possible to incinerate selected liquid wastes as an admixture with oil firing; however, such a practice is not considered feasible for the following reasons:

1. Natural gas and coke oven gas are the preferred fuels in soaking pits.
2. No soaking pits have any type of air pollution control other than good combustion practices.
3. Leaks can occur at the cover of the soaking pit.
4. Fuel switching is practiced in some pits, which requires that fuel/air ratios be adjusted.

4.4.2 Detailed Evaluation of Feasible Processes

Because of their greater potential for hazardous wastes disposal, the following processes are examined in more detail:

- Blast furnaces using oil/tar injection
- Open hearth furnaces

4.4.2.1 Blast Furnaces--

Process description--The blast furnace is a tall, cylindrical, countercurrent flow reactor. Figure 4.4-2 shows a cross section of a typical blast furnace. Iron ore, pellets, sinter, limestone, and coke are charged into the blast furnace from the top. Hot air [780° to 1220°C (1400° to 2200°F)] is introduced at the bottom of the furnace through tuyeres. The coke burns at the tuyere level, and the hot gases rise through the descending mass and transfer the sensible heat to the descending raw materials. A temperature of around 1930°C (3500°F) is attained at the tuyere

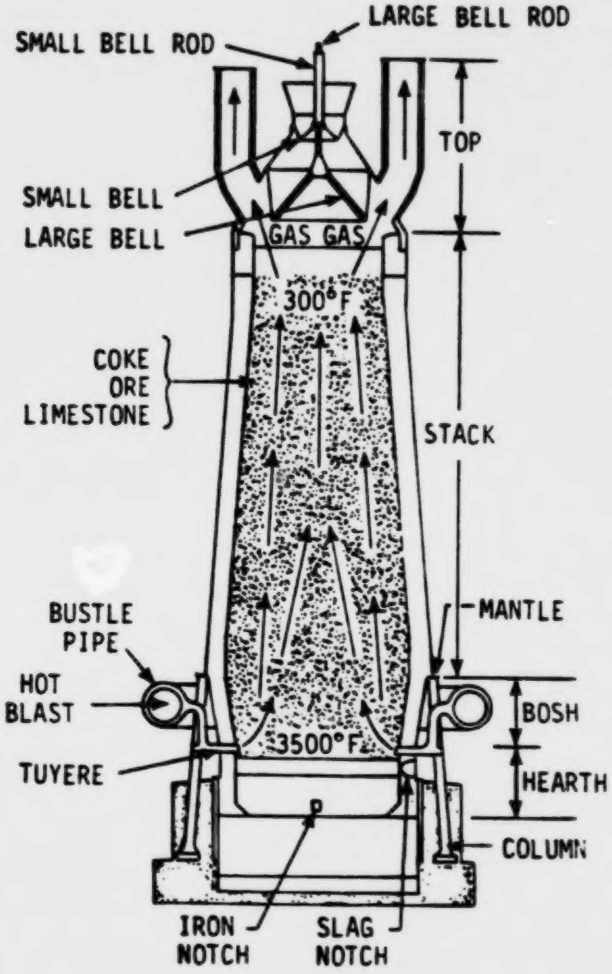
LARGE BELL ROD
SMALL BELL ROD
TOP
SMALL BELL
LARGE BELL
GAS GAS
300°F
COKE
ORE
LIMESTONE
STACK
MANTLE
BUSTLE PIPE
HOT BLAST
BOSH
3500°F
TUYERE
HEARTH
COLUMN
IRON NOTCH
SLAG NOTCH

Figure 4.4-2. Cross section of a blast furnace.

level, and the top gases leave the furnace at around 150°C (300°F). The exit gases pass through a dust catcher (cyclone) and then through a scrubber system. Part of this thoroughly cleaned gas is fired in the blast furnace stoves for preheating the combustion air. The molten iron accumulates in the hearth, and the lighter slag forms a layer on top of the molten iron. Iron and slag are periodically drained from the furnace.

Uniform raw material size and chemical consistency play a major role in achieving high productivity and trouble-free operations. The raw material requires extensive preparation to achieve proper consistency of size and chemical composition. A systematic pattern of charging different raw materials is practiced to achieve uniform distribution inside the furnace. It takes approximately 8 hours for the charged raw materials to descend to the hearth zone.

The reactions that take place as the raw materials descend through the furnace are essentially endothermic. Iron ore is progressively reduced to iron oxide (FeO) as the mass descends to the bosh area, where the final reduction to iron (Fe) takes place. A reducing atmosphere is prevalent throughout the descent of the materials in the furnace. Requirements such as uniformly sized burden, reducing atmosphere, and temperature conditions make this process unsuitable for the destruction of solid hazardous wastes by charging such wastes at the top of the furnace. The vapors produced at low temperature would leave with the exit gases without complete incineration.

Technical factors--

Compatibility of hazardous wastes with process fuel--In most blast furnaces in the United States some kind of fuel is injected through the tuyeres to reduce coke consumption and increase productivity. The fuels used for this purpose include oil, tar, pitch, natural gas, coke oven gas, and pulverized coal or combinations thereof. Selection is governed by availability and cost.

Table 4.4-1 shows the pattern of injected fuel usage in U.S. and Canadian blast furnaces in 1976. Table 4.4-2 indicates the location, capacity, and fuel injection data for blast furnaces in the United States. Figure 4.4-3 shows where these blast furnaces are located. It is technically feasible to cofire selected wastes with the fuel oil or tar injected at the bottom of the blast furnace.

Graphical determination of suitable waste categories--Smooth and trouble-free blast furnace operation with fuel injection requires that the adiabatic flame temperature and blast volume be kept as constant as possible. In a typical operation the flame is maintained at a temperature of 1870° to 2040°C (3400° to 3700°F)[41] and a blast volume of 1720 Nm^3/min per ton (60,000 scfm per ton) of hot metal. Pertinent process conditions for determining the time-temperature relationship in blast furnaces are based only on the lower portion of the furnace; it is assumed that about one-third of the furnace volume lies below an imaginary line where the gas temperature drops below 1090°C (2000°F). For purposes of constructing a time-temperature profile, it is conservatively assumed that the upper portion of the furnace will be inactive in destroying hazardous compounds. The process conditions for the lower zone are:

Volume of furnace	589 m^3 (20,800 ft^3) (1/3 of total)
Gas volumetric flow rates	5150 Nm^3/min (196,000 scfm) (1.4 x blowing rate)
Maximum reaction zone temperature	1870°C (3400°F)
Exit gas temperature	1090°C (2000°F)

The resulting process curves (plots of Δt and $\Delta \bar{t}$ versus T) are overlaid on the hazardous waste plots in Figure 4.4-4.

Table 4.4-3 indicates the categories of wastes that can be dissociated in the blast furnace. The high flame temperature maintained at the tuyeres and the relatively long residence time

TABLE 4.4-1. USE OF VARIOUS FUELS INJECTED INTO THE BLAST FURNACE IN THE UNITED STATES AND CANADA DURING 1976[38]

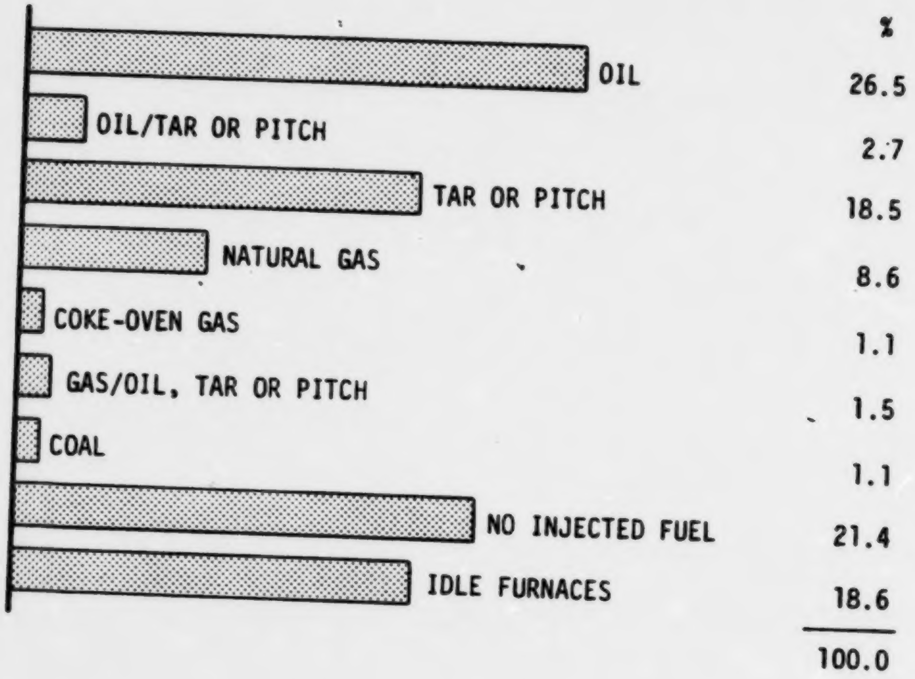

TABLE 4.4-2. BLAST FURNACES IN THE UNITED STATES[39,40]

Company	Location	No. of blast furnaces	Capacity, 10^6 Mg (10^6 tons)	Fuel injection
Armco, Inc.	Ashland, Kentucky	2	1.8 (2.0)	Coal/O_2[a]
	Houston, Texas	1	0.7 (0.8)	Natural gas
	Middletown, Ohio	1	1.8 (2.0)	Natural gas
	Hamilton, Ohio	2	1.8 (2.0)	Tar in one furnace
Bethlehem Steel	Bethlehem, Pennsylvania	4	3.2 (3.5)	-[b]
	Burns Harbour, Indiana	2	3.2 (3.5)	-
	Lackawanna, New York	6	3.8 (4.2)	-
	Sparrows Point, Maryland	5	5.7 (6.3)	-
CF&I Steel Corp.	Pueblo, Colorado	4	0.9 (1.0)	Oil/tar
Crucible Steel	Midland, Pennsylvania	2	0.9 (1.0)	-
Cyclops Corp. Empire-Detroit Division	Portsmouth, Ohio	1	0.6 (0.7)	Oil
Ford Motor Co.	Dearborn, Michigan	3	2.0 (2.2)	Natural gas/O_2
Inland Steel Co.	Indiana Harbour Works East Chicago, Illinois	9	5.9 (6.5)	Oil/tar
Interlake, Inc.	S. Chicago, Illinois	2	1.1 (1.2)	-
Jim Walter Resources, Inc.	Birmingham, Alabama	1	0.4 (0.4)	-
J&L Steel	Aliquippa, Pennsylvania	5	3.3 (3.6)	Oil/O_2
	Cleveland, Ohio	2	1.6 (1.8)	Oil
	E. Chicago, Indiana	4	3.2 (3.5)	-
Kaiser Steel	Fontana, California	4	2.5 (2.7)	-
Lone Star Steel	Lone Star, Texas	1	0.4 (0.4)	-
McLouth Steel Corp.	Trenton, Michigan	2	1.5 (1.7)	-

(continued)

TABLE 4.4-2 (continued)

Company	Location	No. of blast furnaces	Capacity, 10^6 Mg (10^6 tons)	Fuel injection
National Steel	Granite City, Illinois	2	1.6 (1.8)	Oil/O_2
	Great Lakes Steel Div., River Rouge, Michigan	4	3.4 (3.7)	Gas/oil/O_2
	Hanna Furnaces, Buffalo, New York	3	0.6 (0.7)	Oil in one furnace
	Weirton Steel Division, Weirton, West Virginia	4	2.7 (3.0)	Oil/tar/pitch
Republic Steel Corp.	Buffalo, New York	2	0.7 (0.8)	-
	Cleveland, Ohio	5	2.7 (3.0)	-
	Gadsden, Alabama	2	0.3 (0.8)	-
	S. Chicago, Illinois	1	1.13 (1.25)	-
	Warren, Ohio	1	1.13 (1.25)	-
	Youngstown, Ohio	3	2.2 (2.4)	-
Sharon Steel Corp.	Sharon, Pennsylvania	2	0.9 (1.0)	-
Shenango, Inc.	Neville Island, Pennsylvania	2	0.4 (0.4)	-
U.S. Steel Corp.	Braddock, Pennsylvania	4	2.3 (2.5)	-
	Duquesne, Pennsylvania	2	1.4 (1.5)	-
	Fairfield, Alabama	6	2.4 (2.7)	-
	Fairless Hills, Pennsylvania	3	2.4 (2.7)	-
	Gary, Indiana	11	5.9 (6.5)	-
	Geneva, Utah	3	1.8 (2.0)	-
	Lorain, Ohio	5	2.4 (2.7)	-
	McKeesport, Pennsylvania	2	0.3 (0.3)	-
	Rankin, Pennsylvania	2	1.8 (2.0)	-
	S. Chicago, Illinois	5	3.7 (4.1)	-
	Youngstown, Ohio	4	1.4 (1.6)	-
Wheeling - Pittsburgh Steel	Monessen, Pennsylvania	3	1.4 (1.5)	-
	Steubenville, Ohio	5	2.2 (2.4)	-

[a] O_2 = Oxygen.

[b] Dash means no information available.

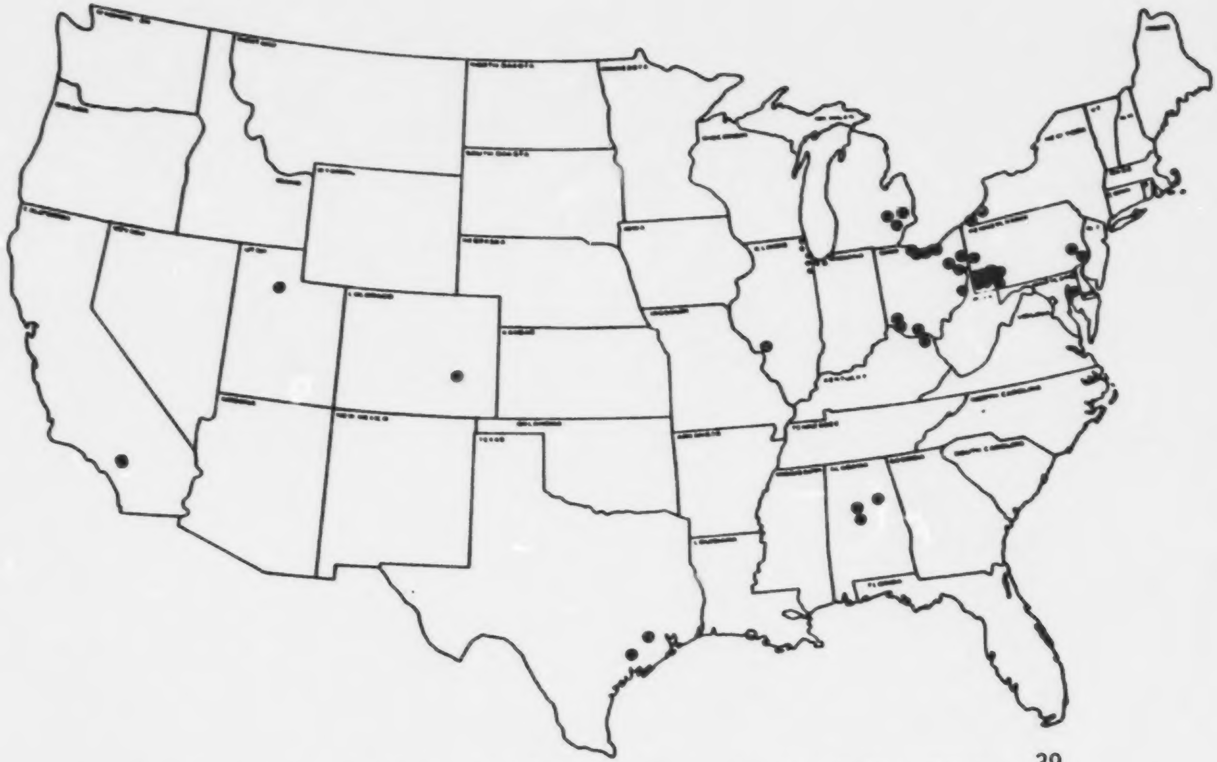

Figure 4.4-3. Location of blast furnaces in the United States.[39]

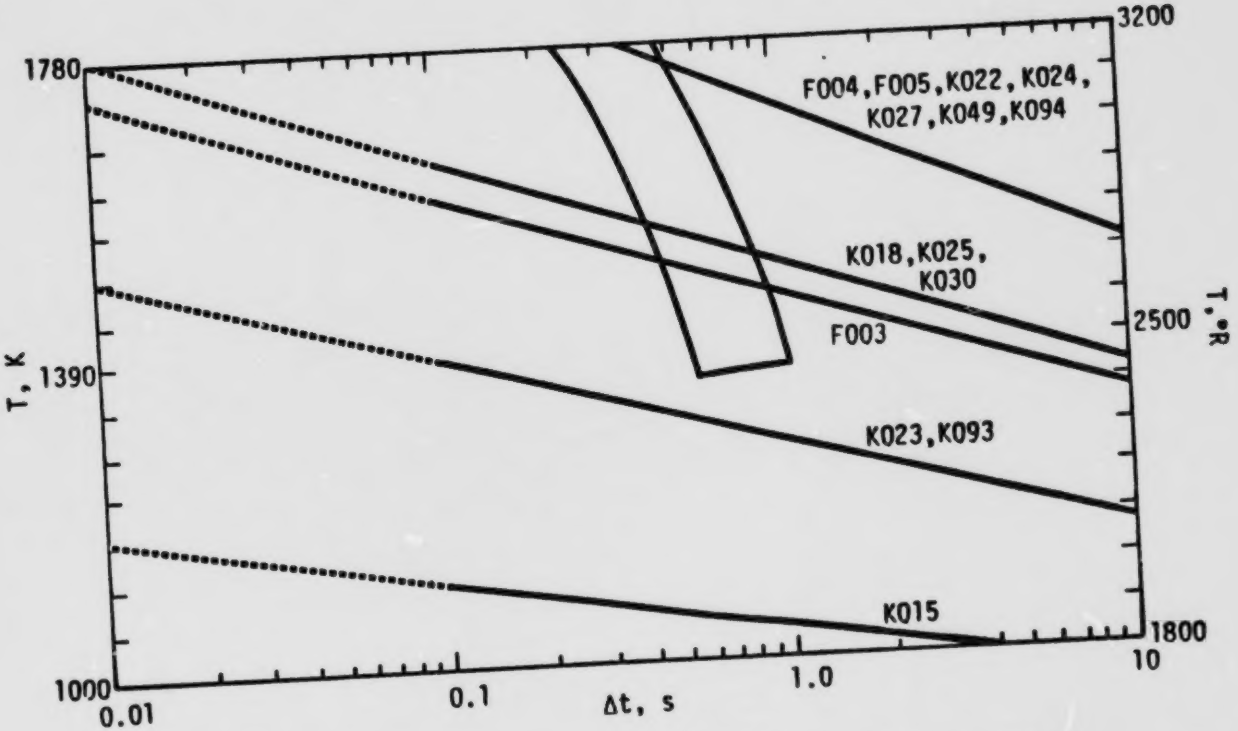

Figure 4.4-4. Hazardous waste destructibility predictions for blast furnaces in iron and steel manufacture.

provide conditions suitable for the thermal destruction of most K and F Series wastes. The reason for excluding some of the wastes is given in the remarks column.

TABLE 4.4-3. APPLICABILITY OF BLAST FURNACES FOR THERMAL DESTRUCTION OF HAZARDOUS WASTES

Type of wastes	Applicability	Remarks
K015	No	Highly chlorinated compounds
K023	Yes	
K093	Yes	
F003	Yes	
K018	No	Highly chlorinated compounds
K025	No	Organic sludge
K030	No	Chlorinated
F004	Yes	
F005	Yes	
K022	No	Sludge
K024	No	Sludge
K027	No	Chlorinated sludge
K049	No	Aqueous sludge
K094	No	Sludge

Effects on product quality and product application--The only impact on iron or slag composition would be from metals or inorganics in the waste. Most of the elements that form stable oxides (aluminum, calcium, titanium) will be taken up by the slag. For the most part, metals such as iron, manganese, and chromium will be dissolved in the molten iron. In either case, the contribution of metals from the waste categories under consideration is expected to be insignificant and to have no measurable effect on the iron or slag. Sulfur-containing wastes should be avoided, however, because sulfur is an undesirable element in the iron.

Impact on process hardware--The dissociation products in the reaction zone at the tuyeres are carbon oxide, hydrogen, nitrogen, and a variety of volatile metal oxides, halides, and sulfides, depending on the composition of the hazardous wastes. Volatile metallic species can form at intermediate to high temperatures in the blast furnace. The most troublesome are zinc, lead, and alkali metal oxides. The volatile species formed at the lower level in the furnace ascend to the cooler portions of the furnace where condensation and readsorption can occur. In this case, a recirculating load is established with increasing concentration of volatile species, which eventually leads to discharge of these species in the off-gases or slag-metal system. The condensation of large amounts of alkali metals and halides in the cooler part of the furnace can lead to sticking and bridging and thus impede the smooth flow of materials in the blast furnace. In addition, the alkali and halides attack the refractory lining of the furnace, which leads to physical deterioration of the lining and reduced lining life. Lead and zinc deposits also can cause refractory damage; great care is taken to avoid these metals in the feed to blast furnaces.

Most furnaces have scrubbers with recirculating water systems. Inorganic residuals originating from hazardous wastes, particularly alkali metal salts and volatile metal salts, might increase the load on the scrubber water in these systems and make it necessary to increase blowdown rates. The blast furnace is normally the keystone of steel mill operation. Because upsets in operation can be disastrous and can require days or weeks for recovery, injection of wastes would have to be done very cautiously.

Acceptable amounts of hazardous waste feed--The oil injection rates achieved in the industry vary widely according to the individual practices followed. The highest reported consumption is around 115 kg/Mg (230 lb/net ton) of hot metal (maximum) and 90 kg/Mg (180 lb/net ton) on the average.[42] Assuming that 25 percent of the furnaces using oil or tar injection could burn 9 to 14 kg (20 to 30 lb) of liquid wastes per ton of hot metal (or 10 to 15 percent of it), it is estimated that 180,000 to 270,000 Mg/yr (200,000 to 300,000 tons/yr) of liquid wastes could be disposed of in blast furnaces. This is based on 79 million Mg (87 million tons) of iron produced in 1979 in the U.S. steel industry.

Provisions for waste introduction--Oil is generally pumped through a separate lance introduced through the tuyere. Steam or air may be used to atomize the oil. A typical lance design consists of two concentric pipes. Oil flows through the central pipe and steam goes through the outer pipe.

Oil is generally stored in a storage tank near the furnace, which is equipped with a heating and pumping system for delivery to the individual injection lances. Wastes could be mixed with the oil prior to injection. Use of a separate lance is possible, but this would require new blast pipes at each tuyere and a separate control system.

Projected trends in process fuels--Coke consumption in blast furnaces has steadily declined over the past 20 years because of improved burdens, higher blast air temperatures, and the use of fuel injection. Although fuel injection is expected to continue as a common practice, the trend is towards the replacement of several smaller furnaces with a few larger furnaces. Consequently, the total number of blast furnaces is declining. With iron production assigned to fewer furnaces, upsets or delays in the operation become more critical. This will tend to discourage such auxiliary operations as hazardous waste injection.

Geographic matching of industry locations and waste generators--The generation of wastes in categories F003, F004, and F005 is widespread in industrial areas. As Figure 4.4-3 shows, most of the blast furnaces also are located in the industrialized states. Category K023 wastes are generated in Illinois, Pennsylvania, and New Jersey, and K093 wastes are generated in Illinois, Texas, New Jersey, and California. Thus, the geographical matching between waste sources and blast furnaces is reasonably good.

Environmental factors--The effluent streams from a blast furnace include slag, off-gases, scrubber water blowdown, and fugitive emissions during casting. The slag is normally sold as a byproduct for use as aggregate. Although ash components and certain metallic oxides in the waste could find their way into the slag, the amounts would probably be small and have no significant effect on the slag leaching characteristics.

Blast furnaces are equipped with high-efficiency ($\Delta P = 15$ to 17 kPa) scrubbers. The off-gases are cleaned to 0.023 g/m^3 (0.01 gr/ft^3) or better for use as a byproduct fuel in the stoves and boilers and for other uses. The gas has a heating value of about 3.4 MJ/m^3 (90 Btu/ft^3); therefore, gaseous compounds formed from the destruction of hazardous wastes would be further exposed to combustion conditions. Because excess gas is sometimes bled to the atmosphere, the off-gases would have to be monitored during test burns to determine what compounds could be expected in them.

Most furnaces are equipped with recirculating scrubber water systems. These systems must meet stringent blowdown rates to comply with guideline discharge limitations for effluents. Any increase in chlorides resulting from waste destruction would necessitate an increase in the blowdown rates.

Fugitive emissions can occur at the top of the furnace as a result of leaking seals in the charging system or sudden increases in furnace pressure. Normally these releases involve relatively small amounts of off-gas. The casting and flushing of slag are more common sources of fugitive emissions. Because gases escape from the tap hole, injection would have to be stopped during these operations. If wastes are used, close attention would have to be given to the injection system. This would require instrumentation for monitoring the flow at each tuyere and automatic shutoff valves. Auxiliary lances and related equipment require frequent inspection and maintenance to avoid plugging, leaks, and blowouts. No fugitive emissions are associated with oil injection.

Economic factors--Fuel injection is done for economic reasons; it increases productivity and reduces coke consumption. Any credits for the use of hazardous wastes would be an added incentive. Hazardous wastes with high Btu values could replace part of the injected fuel and thus provide an economic incentive.

Special considerations--Halogenated wastes and wastes containing alkalies should be avoided completely because they would have an adverse effect on the blast furnace lining. Similarly, wastes with a high-sulfur content should be avoided because sulfur is an undesirable element in the metal product. The safety precautions necessary in the receiving, storage, handling, and atomizing of liquid hazardous wastes would have to be meticulously followed.

Institutional factors--In general, steelmaking facilities are not likely to accept hazardous wastes for incineration. Labor unions may object on the grounds of worker exposure to the hazardous wastes. Inasmuch as the industry has invested heavily in air and water pollution controls to treat its own waste streams, it is not likely to consider the introduction of new potential environmental problems. In addition, the decreases in productivity associated with the handling, storage, and destruction of hazardous wastes would not be consistent with the industry's goal to increase productivity. Moreover, most steel plant facilities are close to population centers, which means potential adverse community impacts would have to be considered. One steel plant considered experimenting with incineration of PCB's by injection through the tuyeres in a blast furnace and later evaluated the use of a kiln, but both plans were eventually rejected.[43]

4.4.2.2 Open Hearth Furnaces--

Process description--Open hearth (OH) furnaces are used to refine scrap and hot metal into steel. Up to 100 percent steel scrap or a combination of scrap and molten iron can be charged in this versatile process. Limestone and fluorspar are used as fluxes to absorb impurities. Fuels (coke oven gas, natural gas, oil, tar, or a combination of gas and liquid fuel) are alternately fired from both ends of the furnace. As the combustion gases pass through brick checkerwork, they impart sensible heat to the brickwork. The incoming combustion air is preheated by passing it through the checkerwork. Approximately every 30 minutes, the firing is reversed to recover the heat through the brickwork. Many OH furnaces are equipped with waste heat boilers to conserve energy. The exit gases are first cleaned in either electrostatic precipitators or scrubbers and then exit through the stack. Figure 4.4-5 shows a cross section of an open hearth furnace.

The scrap and flux are charged into the furnace through the doors of specially designed charging boxes. The hot metal is poured into the furnace through the hydraulically operated doors by means of a hot metal chute. Steel and slag are tapped from the tap hole at the rear of the furnace opposite the charging doors. Tap-to-tap time, which varies from 6 to 12 hours, depends on the ratio of hot metal and scrap and the use of oxygen. Productivity has increased with the advent of oxygen lancing through the roof, which hastens the refining process. The operating OH furnaces in integrated steel plants have capacities ranging from 250 to 420 tons per heat. Table 4.4-4 lists currently operating furnaces in the United States. Figure 4.4-6 shows the location of these furnaces. No new OH furnaces are being constructed, and many are being phased out because of the high cost of production per ton of steel and lower productivity compared with basic oxygen furnaces. Once the major method for steel production in the United States, OH furnaces accounted for only 1.7 percent of total production in 1980.

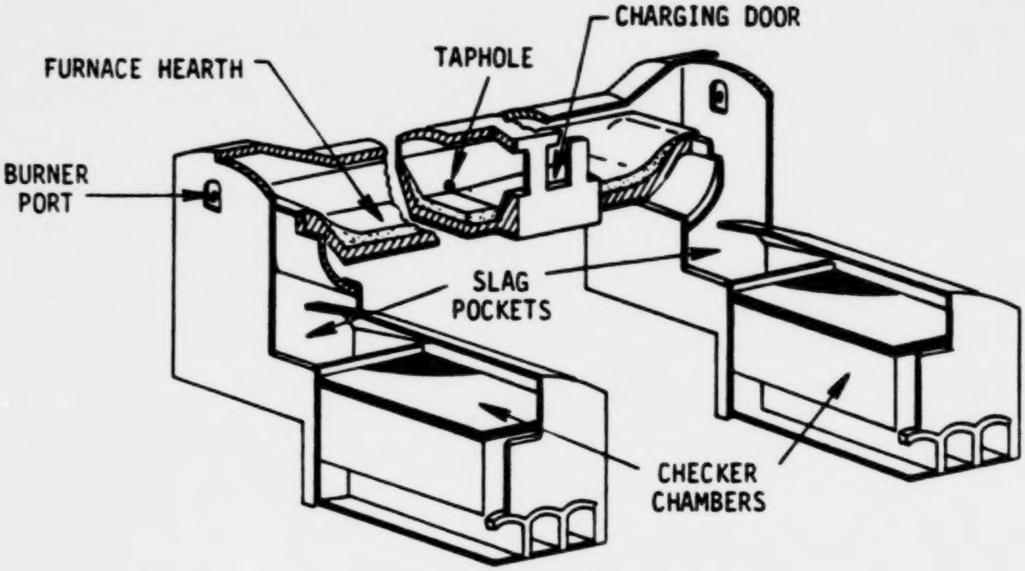
CHARGING DOOR
FURNACE HEARTH
TAPHOLE
BURNER PORT
SLAG POCKETS
CHECKER CHAMBERS

Figure 4.4-5. Cross section of an open hearth furnace.

TABLE 4.4-4. LIST OF OPEN HEARTH FURNACES IN THE UNITED STATES[39,42]

Company	Location	Number of furnaces	Annual capacity, 10^6 Mg (10^6 tons)
Armco, Inc.	Middletown, Ohio	6	1.11 (1.225)
Bethlehem Steel Corp.	Sparrows Point, Maryland	7	3.2 (3.50)
Inland Steel Co.	East Chicago, Illinois	7	2.2 (2.40)
Lone Star Steel Co.	Lone Star, Texas	5	1.4 (1.50)
Pacific States Steel	Union City, California	4	0.45 (0.50)
United States Steel Corp.	Fairless Hills, Pennsylvania	9	3.3 (3.60)
	Homestead, Pennsylvania	11	4.2 (4.60)
	Geneva, Utah	10	2.5 (2.75)

Two methods of hazardous waste destruction can be considered in OH furnaces:

1. Liquid wastes having high Btu value could be cofired with oil or tar.

2. Highly viscous, semisolid wastes could be charged into the furnace through the doors.

Technical considerations--

Graphical determination of suitable waste categories-- Pertinent process conditions for determining the time-temperature relationship in open hearth furnaces are:

Volume of furnace	200 m^3 (7000 ft^3)
Gas volumetric flow rate	790 Nm^3/min (30,000 scfm)
Maximum reaction zone temperature	1790°C (3250°F)
Exit gas temperature	1480°C (2700°F)

Figure 4.4-7 presents a temperature profile for a typical open hearth furnace. Figure 4.4-8 shows a time-temperature curve for a typical OH furnace overlaid on the hazardous waste plots. A flame temperature of around 1930°C (3500°F) is achieved in OH furnaces. Coupled with a retention time of 2 to 3 seconds, this temperature is suitable for destroying several hazardous wastes.

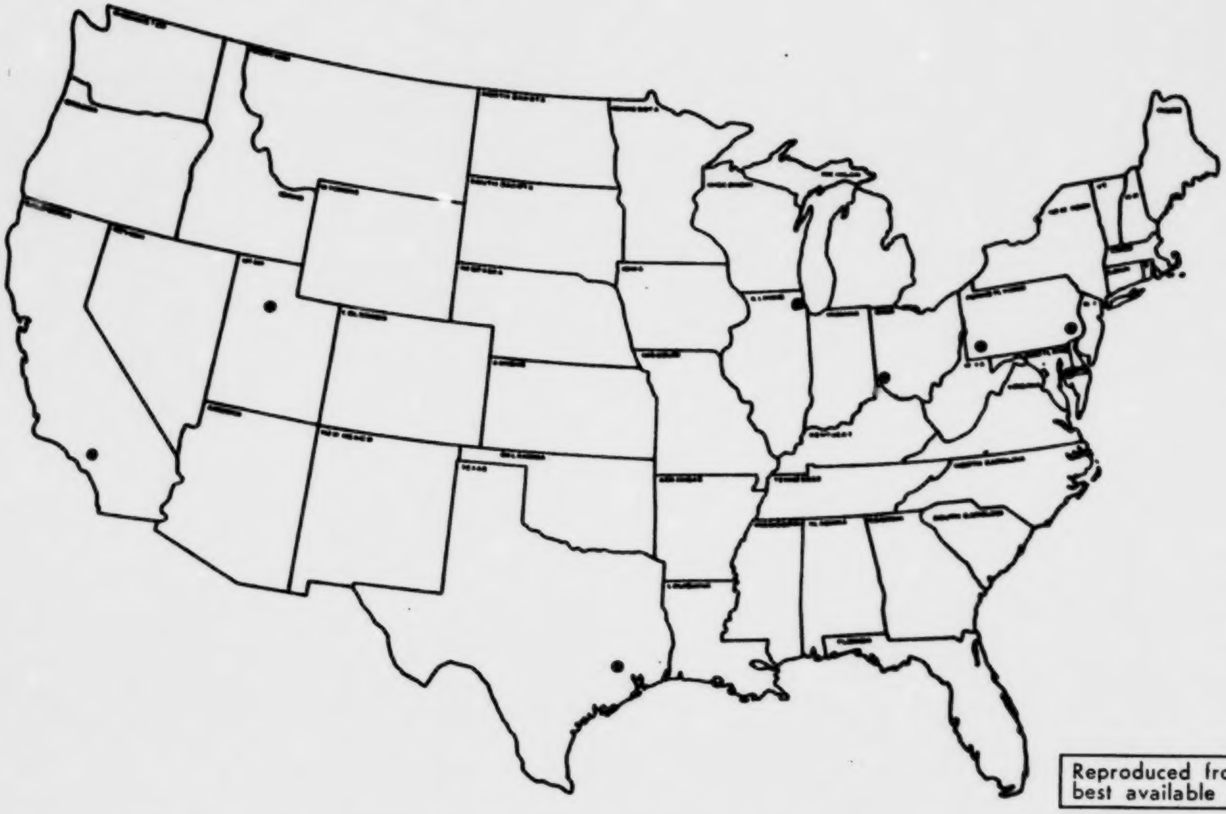

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Figure 4.4-6. Location of open hearth furnaces in the United States.[39]

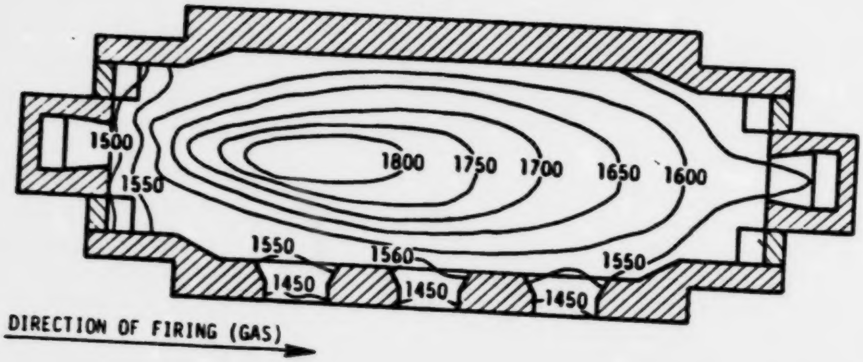
1500
1550
1800
1750
1700
1650
1600
1550
1560
1550
1450
1450
1450
DIRECTION OF FIRING (GAS)

Figure 4.4-7. Temperature profiles within a typical open-hearth furnace.[44]

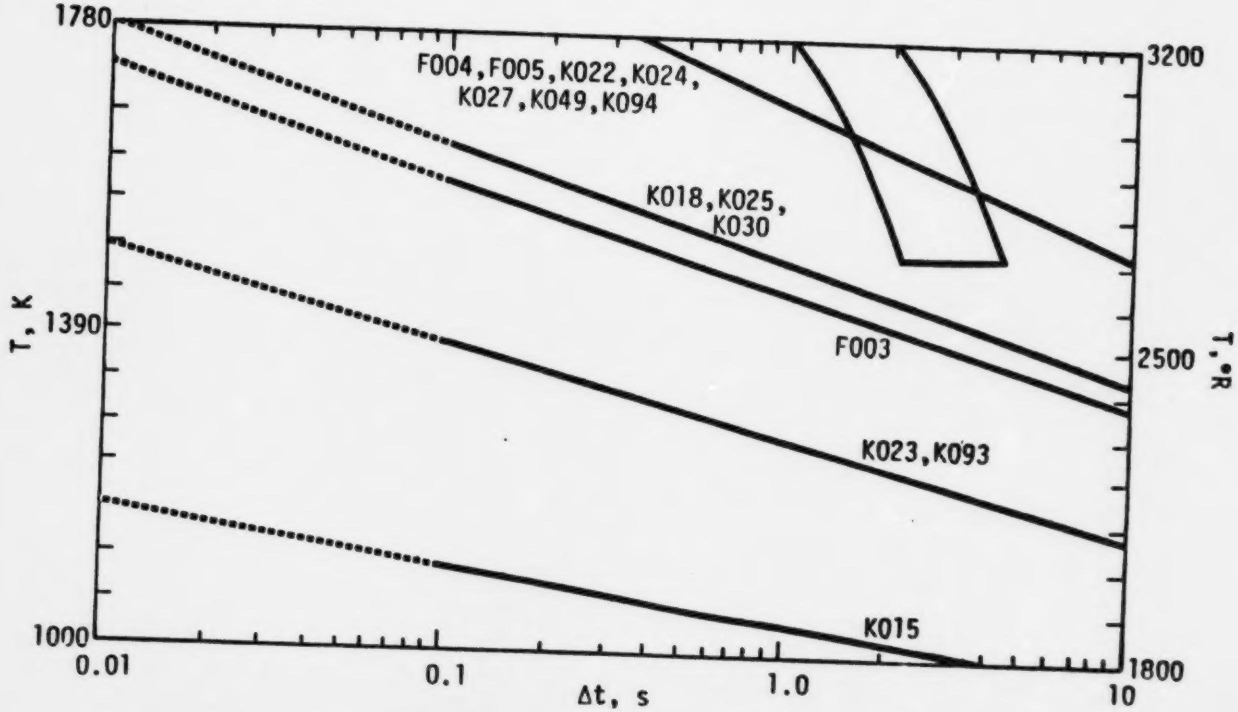

Figure 4.4-8. Predictions of hazardous waste destructibility in open-hearth furnaces in steelmaking.

Gases generated farthest from the burner will travel through the checkerwork, where the temperature is still sufficiently high [1150° to 1210°C (2100° to 2200°F)][43] to complete destruction.

Effects on product quality and product application--Table 4.4-5 shows the distribution of elements between slag and metal in the OH furnace process, based on oxygen potential. When present in slag, the elements are in their oxide or sulfide form. Relatively small amounts of elements such as Cn, nickel, or antimony significantly affect steel properties. Any waste would therefore have to be monitored for the presence of such tramp elements before being accepted.

TABLE 4.4-5. DISTRIBUTION OF CONTAMINANT ELEMENTS BETWEEN SLAG AND METAL[44]

Group 1 - Elements almost completely taken up by slag: Si, Al, Ti, Zr, B, and V; Ca, Mg

Group 2 - Elements distributed between slag and metal: Mn, P, S and Cr

Group 3 - Elements almost completely in solution in metal: Cu, Ni, Sn, Mo, Co, W, and probably As and Sb

Group 4 - Elements out of slag and metal: Zn, Cd, Pb, and Ag and Hg

The small amounts of contaminants that would normally combine in the slag are not expected to have an adverse effect on slag properties. On occasions when slag is recycled to the blast furnace, lead and zinc would have to be monitored. As in the case of the blast furnace, sulfur-bearing wastes would be unacceptable.

Impact on process hardware--Most open hearth furnaces have a basic refractory lining. The basic slag contains a high percentage of calcium oxide, which would promote retention of heavy metal oxides that may be generated during disposal of some wastes.

The operating OH furnace shops in the United States are equipped with either high-efficiency electrostatic precipitators or venturi scrubbers. Gaseous removal efficiencies in ESP's are negligible; however, venturi scrubbers can collect a portion of the gaseous pollutants, particularly halogens. As discussed under blast furnace fuel injection, both halogenated wastes and wastes containing alkali metals should be avoided because they could reduce the life of the refractory lining. Lead and tin residuals also should be avoided because they, too, adversely affect the lining life.

Acceptable amounts of hazardous waste feed--Fuel consumption in OH furnaces varies according to the proportions of scrap and hot metal charged. A typical value for a 50/50 charge is 2.9 GJ/Mg (2.5 x 10^6 Btu/ton). In a 180-Mg (200-ton) oil-fired furnace, this is equivalent to about 13,200 liters (3500 gallons) of oil per heat. Assuming a substitution rate of 10 percent for hazardous waste fuel, about 6.4 liters (1.7 gallons) of waste could be consumed per ton of steel. Given an annual steel production rate in OH furnaces of 12 x 10^6 Mg (13 x 10^6 tons), the maximum potential waste disposal rate would be 83 x 10^6 liters (22 x 10^6 gallons per year). The actual potential is probably closer to half this rate, however, because wastes could not be fired during charging operations or periods of bath turbulence. Furthermore, not all furnaces could accommodate this practice.

Provision for waste introduction--Fuel oil and tar are stored near the furnace building in storage tanks equipped with a heating and pumping system to individual furnaces. Wastes could be stored in a separate tank and metered into the fuel before it reaches the burner. If the waste is cofired with coke oven gas or natural gas, burner modifications would have to be made to the furnace and separate waste fuel lines would have to be provided from the storage tank to the furnace(s).

Projected trends in process fuel--No major shifts in process fuel use are expected in the OH furnace process. As discussed previously, however, the use of the OH furnaces is declining. Existing shops will continue to operate as long as they are economical, but they will be retired as they near the end of their useful life and will not be replaced.

Geographical matching of industry locations and waste generators--Table 4.4-6 presents the categories of liquid wastes that probably can be destroyed in open hearth furnaces, based on the predictions from Figure 4.4-8. Categories K023 and K024 are generated in the States of Pennsylvania, Illinois, and New Jersey; K093 and K094 are generated in Illinois, Texas, New Jersey, and California; generation of F003, F004, F005, K022, and K049 is widespread. Waste categories K015, K018, K027, and K030 are shown as not applicable because the chlorinated compounds will deteriorate the furnace refractory. Based on the distribution shown in Figure 4.4-6, there is some degree of matching between waste generators and open hearth furnace locations. The limited number of furnaces overall, however, rules out widespread national application.

TABLE 4.4-6. APPLICABILITY OPEN HEARTH FURNACES FOR THERMAL DESTRUCTION OF HAZARDOUS WASTES

Waste category	Applicability	Remarks
K015	No	Highly chlorinated
K023	Yes	
K093	Yes	
F003	Yes	
K018	No	Heavily chlorinated organics
K025	Yes	
K030	No	Chlorinated
F004	Yes	
F005	Yes	
F022	Yes	
F024	Yes	
K027	No	Chlorinated sludge
K049	Yes	
K094	Yes	

Environmental factors--Fugitive emissions during charging of raw materials and emissions through the doors during flame reversal are potential problems. Waste injection would have to be cut off during charging and periods of bath turbulence. Furnace pressure would have to be controlled at near zero or slightly negative to avoid puffs of fugitive emissions, which is counter to the normal practice of maintaining furnace pressure at zero to slightly positive. Any residues left after destruction of the hazardous waste would enter the metal or the slag. The slag could be handled in the normal manner, but heavy metal concentrations in slag, scrubber sludge, and ESP dust would have to be monitored closely.

Economic factors--Fuel costs are not an overwhelming factor in the total cost structure of open hearth steelmaking. Although fuel credits from high-Btu wastes could be used, it is doubtful they could affect total costs significantly. There is a potential for converting retired shops into waste facilities operated independently of the steelmaking operation by other entrepreneurs. Analysis of such a scenario, however, is beyond the scope of this study.

Institutional factors--Considerable resistance can be expected to the acceptance of hazardous wastes into the open hearth furnaces. The operating open hearth furnaces are competing to remain in business, and productivity and quality are of prime consideration. This factor may preclude any consideration of hazardous waste destruction in these furnaces.

4.5 LIGHTWEIGHT AGGREGATE INDUSTRY

Lightweight aggregates encompass a variety of raw materials that provide the bulk in concrete products. They are distinguished from other mineral aggregate materials by their ability to deliver strength with less dead load.[45,46] The various lightweight aggregate materials can be classified as follows:[45]

- Natural lightweight aggregates - Prepared by crushing and sizing pumice, volcanic cinders, tuff, scoria, and breccia.
- Byproduct lightweight aggregates - Prepared by crushing and sizing foamed and granulated slag, coke breeze, and cinders.
- Manufactured structural lightweight aggregates - Prepared by pyroprocessing clay, shale, or slate in rotary kilns or on traveling grate sintering machines.

This section focuses on the pyroprocessing of expandable clay, shale, or slate to produce manufactured structural lightweight aggregates. Estimates indicate that the rotary kiln method is used in the production of 80 percent of all structural lightweight aggregates.[47]

4.5.1 Process Descriptions

4.5.1.1 The Rotary Kiln Method--

In most cases, the lightweight aggregate plant is composed of a quarry, a raw material preparation area, a kiln, a cooler, and a product storage area. These facilities are usually located on a tract of land that contains a quarry and encompasses several hundred acres.[48] Figure 4.5-1 provides a flow diagram of a lightweight aggregate plant.

The first step in the manufacture of lightweight aggregate is to establish a plant on a tract of land that has suitable raw material. Only some deposits of clay, shale, or slate have the desired characteristic of bloating. The raw material must be expandable and contain small quantities of gas producing compounds.[49] The clay, shale, or slate is mined in the quarry and then transferred to the raw material preparation area. These areas vary from plant to plant, but they generally include drying, crushing, stock piling, final reduction, and sizing.[50]

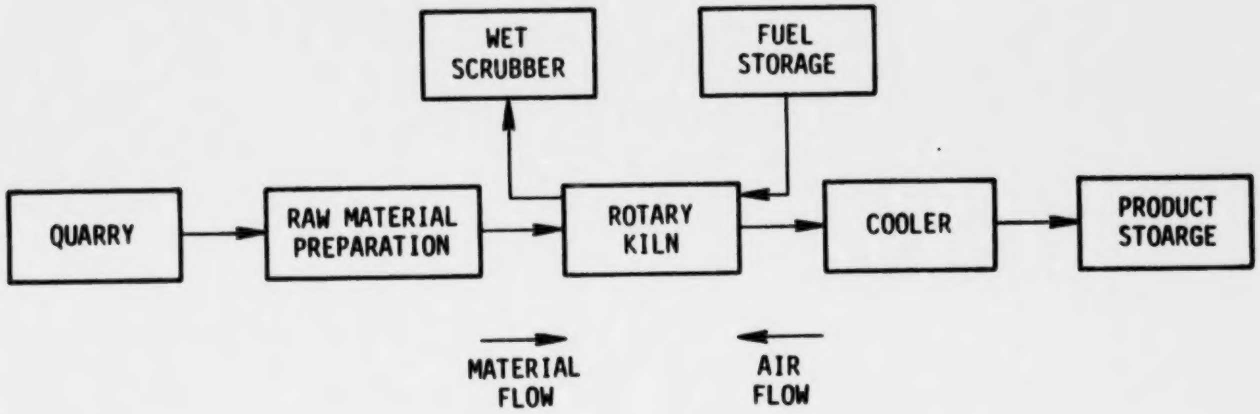
WET SCRUBBER
FUEL STORAGE
QUARRY
RAW MATERIAL PREPARATION
ROTARY KILN
COOLER
PRODUCT STOARGE
MATERIAL FLOW
AIR FLOW

Figure 4.5-1. Flow diagram of a modern lightweight aggregate plant.

After it has been prepared, the sized raw material is sent by conveyor to the kiln for firing. The rotary kiln is the heart of a lightweight aggregate plant. Figure 4.5-2 is a diagram of a modern lightweight aggregate rotary kiln. As the figure shows, the kiln is a refractory-lined, cylindrical, steel furnace equipped with an electrical drive that rotates it at 2 to 3 rpm.[51] Typically, its dimensions are 3.7 to 4.6 m (12 to 15 feet) in diameter by 46 to 61 m (150 to 200 feet) in length.[48,51] The kiln is slightly inclined to the horizontal so that material fed onto the upper end travels slowly by gravity until it discharges into the cooler at the lower end. The burners, located at the discharge end, can accommodate natural gas, fuel oil, pulverized coal, or a combination thereof.[51,52]

The dry raw material fed into the kiln is initially preheated by hot combustion. When it leaves the preheating zone, the raw material enters a second zone, where it melts to a semiplastic state and begins to generate gases which serve as the bloating agent. In this zone, specific compounds (hematite, calcite, dolomite, pyrites, and lemonite) begin to decompose and form gases such as SO_2, CO_2, SO_3, and O_2 that eventually trigger the desired bloating action.[49] As temperatures reach their maximum [~1150°C (~2100°F) for clay and ~1210°C (~2200°F) for shale or slate] in the firing or bloating zone, the semiplastic raw material becomes sufficiently viscous to contain the expanding gases. This bloating action produces a mass of small, unconnected air cells, which the material retains after it cools and solidifies.[47]

Such kiln operating parameters as flame temperature, excess air, feed size, material flow, and speed of rotation vary from plant to plant and are determined by the general characteristics

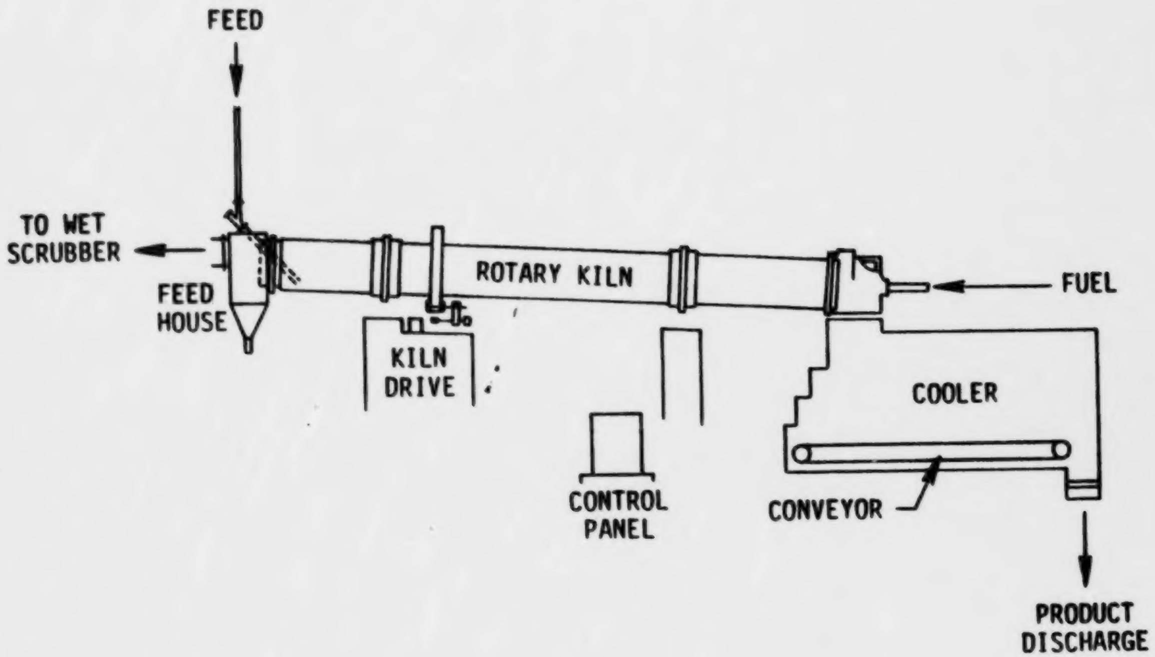
FEED
TO WET SCRUBBER
FEED HOUSE
KILN DRIVE
ROTARY KILN
CONTROL PANEL
FUEL
COOLER
CONVEYOR
PRODUCT DISCHARGE

Figure 4.5-2. Lightweight aggregate rotary kiln and cooler.[53]

of the raw material. Maximum temperatures in the rotary kiln vary from 1120° to 1260°C (2050° to 2300°F), depending on the type of raw material being processed and its moisture content.[48,51] Exit temperatures may range from 150° to 650°C (300° to 1200°F), again depending on the raw material and on the kiln's internal design.[48,51] Approximately 80 to 100 percent excess air is forced into the kiln to aid in expanding the raw material.[51]

Originally, most lightweight aggregate plants were small, loosely run operations that used secondhand equipment from other industries.[51] Some of these marginal plants have ceased operations because of low productivity and rising energy and pollution control costs, whereas others have increased their productivity.[51] Approximately 50 to 80 percent of the remaining lightweight aggregate plants have modernized.[51] Some kilns (approximately 50 percent) have incorporated such internal design features as lifters, dams, and heat exchangers to modify the retention time of raw materials, to control the heat transfer over the length of the kiln, and to reduce energy costs.[52,53] Coolers also have been added to reduce energy costs and simultaneously increase productivity. The number of kilns at a lightweight aggregate plant varies from one to six. The industry appears to be moving toward large-volume, high-efficiency plants, which can be more profitable.[54]

The design of an appropriate burner system is perhaps the most critical feature in the lightweight aggregate rotary kiln.[52] Maintaining the correct relationship between the retention time of the feed and the temperature along the axis of the kiln is essential to achieving the desired product quality. A proper time-temperature relationship ensures that the raw material does not disintegrate or fuse to either adjoining particles or to the kiln's refractory lining. The flame shape and directional control of the flame must provide sufficient heat release to meet the time-temperature requirements while maintaining a material temperature within relatively narrow limits in the bloating zone.[52] A thermocouple assembly is normally installed and monitored in the control room to ensure that appropriate time-temperature requirements are maintained.

4.5.1.2 Sintering Process--

In the sintering process, clay or shale is mixed with pulverized coal and burned.[47] During burning, the raw material on the moving grate expands under controlled conditions. Because of the lower temperatures used in this method [870°C (~1600°F)], sometimes 20 to 30 percent of the burnt material must be remixed with the raw material and reprocessed on the traveling grate.[45,47]

4.5.2 Process Assessment for Hazardous Waste Destruction

The sintering process is not considered further because of its lower temperatures, the brief residence time in the combustion zone, and the difficulty of introducing hazardous waste into the furnace. Only the rotary kiln method for pyroprocessing expandable clay, shale, or slate is investigated. This latter process appears to meet the time, temperature, and turbulence requirements needed for thermal destruction of hazardous wastes.

4.5.2.1 Graphical Determination of Suitable Waste Categories--

Process data for the lightweight aggregate rotary kiln--The residence time (4 seconds, based on maximum temperature) and temperature range [370° to 1150°C (700° to 2100°F)] of a typical lightweight aggregate rotary kiln indicate that destruction of some hazardous waste categories may be feasible.[48] A typical rotary kiln processes approximately 450 Mg (500 tons) of lightweight aggregate per day.[51] This kiln has an average furnace volume of 1000 m^3 (35,343 ft^3) and an average volumetric flow rate of 1920 Nm^3/min (73,170 scfm).[48]

Figure 4.5-3 presents mean and fast-path process curves for the lightweight aggregate rotary kiln. These plots are overlaid on the hazardous waste curves to determine which hazardous waste categories are destructible given the kiln's time-temperature

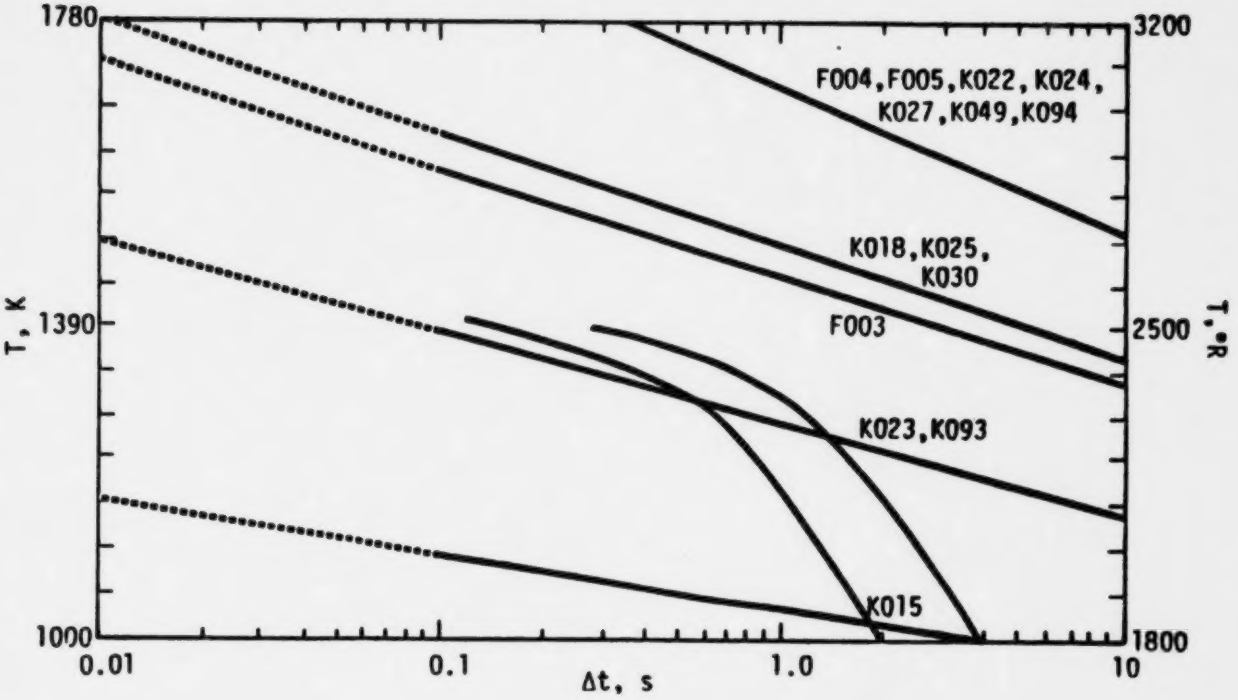

Figure 4.5-3. Hazardous waste destructibility predictions for the lightweight aggregate rotary kiln.

relationship. Based on data from this graph, Table 4.5-1 provides predictions regarding this kiln's ability to destroy completely (99.99%) the selected hazardous waste categories. Because the exit gas temperature is less than the lowest temperature on the graph (Figure 4.5-3), the conservative process line is not shown. Based on the extended case, it appears that waste categories K015, K023, and K093 can be destroyed at the conditions prevailing in this kiln.

TABLE 4.5-1. APPLICABILITY OF THE LIGHTWEIGHT AGGREGATE ROTARY KILN FOR THERMAL DESTRUCTION OF HAZARDOUS WASTES

K015	K023 K093	F003	K018, K025 K030	F004, F005, K022, K024 K027, K049, K095
Yes	Yes	No	No	No

4.5.2.2 Effects on Product Quality and Product Application--

Lightweight aggregate is consumed almost entirely in the construction industry in lightweight concrete or masonry block. It is used in the construction of high-rise complexes and other buildings, ships and barges, bridges and bridge decking, road pavement, and sports tracks.[47] This product has found wide application in the construction industry because of its many advantages over other aggregate materials. These advantages include:[47]

- Lighter weight and greater strength
- Fire resistance
- Thermal insulation and moisture resistance
- Sound insulation
- Wall strength
- Textural finish and workability

The introduction of organic hazardous wastes will have little or no impact on the product quality. The consumption of lightweight aggregate materials is closely linked to construction codes and other specifications dealing with unit weight, size graduations, concrete-making properties, and deleterious substances.[45] The quantities of organic impurities and iron oxide are limited to avoid staining and discoloration. These limits, set by the American Society for Testing and Materials (ASTM), most likely will not be negatively affected by the thermal destruction of hazardous wastes. All of the organic material in the waste should decompose when subjected to the high kiln temperatures.

The introduction of chlorinated wastes could increase dust loading. Some of this dust may precipitate within the kiln. Although chlorinated impurities in the lightweight aggregate will not have an adverse effect on the product, they may have a negative impact on the application of the product. Chlorinated impurities in lightweight aggregate used in cement may cause the setting time of the cement to accelerate.[54] Calcium chloride has been known to have this impact on concrete.

4.5.2.3 Impact on Process Hardware--

A protective coating of material such as that found in cement or lime manufacture is not normally formed on the lightweight aggregate kiln refractory.[52] This lack of a protective coating allows the refractory to be subject to continuous abrasion and to considerable thermal shock during periods of temperature variation. Highly corrosive waste fuels could increase the abrasive damage to the refractory lining.

In addition, the presence of trace quantities of metals and the formation of acids [e.g., hydrogen chloride (HCl)] could cause corrosion of ducting and possibly interfere with the operation of the air pollution control equipment. One company currently incinerating hazardous wastes in these kilns strictly limits both the chlorine and solids content because they believe highly corrosive wastes will have a negative impact on both their wet scrubber and fan.[48]

4.5.2.4 Acceptable Amounts of Hazardous Waste Feed--

According to an industry expert, 3.0 GJ are required to produce 1 Mg of lightweight aggregate in a typical rotary kiln.[51] Based on this estimate and assuming that 10 percent of the required heat input into the kiln can be substituted with hazardous waste fuels, the heat input of hazardous waste can be calculated as:

$$0.10 \times 3.0 \text{ GJ/Mg} = 0.3 \text{ GJ/Mg or } 300 \text{ MJ/Mg of aggregate}$$

It was previously shown that the lightweight aggregate rotary kiln is capable of destroying wastes in categories K015, K023, and K093. By using an average heating value of 20 MJ/kg of waste or 20,000 MJ/Mg (obtained from Table 2-3), the rate of hazardous waste feed can be estimated as:

$$300 \text{ MJ/Mg of aggregate} \times \left(\frac{1}{10{,}000 \text{ MJ/Mg}}\right)$$

$$= 0.015 \; \frac{\text{Mg waste}}{\text{Mg aggregate}}$$

For a typical lightweight aggregate kiln process rate of 450 Mg per day, assuming 260 days per year of operation, the hazardous waste disposal rate is estimated to be 1750 Mg/yr.

4.5.2.5 Trends in Process Fuel Consumption--

The rising cost of natural gas and oil over the last several years has caused the lightweight aggregate industry to turn to coal as the main fuel source.[51] The industry has been looking for cheap alternative fuel sources, as evidenced by the one firm that is already thermally destroying hazardous wastes.[48]

4.5.2.6 Geographical Matching of Industry Locations and Waste Generators--

Figure 4.5-4 shows the distribution of domestic lightweight aggregate plants by state. Texas, North Carolina, Virginia, and California account for 33 percent of these plants.

Table 4.5-2 presents the SIC codes and geographic distribution of the industries generating each category of destructible

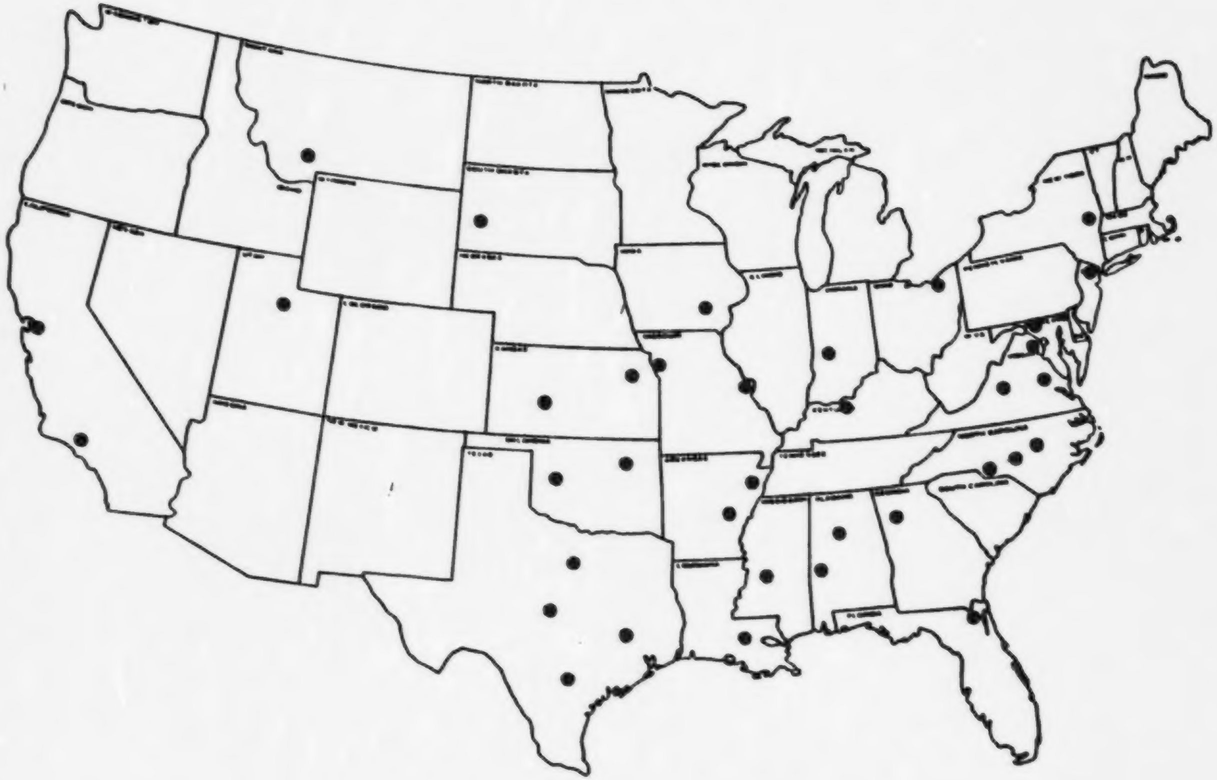

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Figure 4.5-4. Lightweight aggregate plant locations in the United States.[55]

wastes. The areas specifically identified as generating wastes in categories K015, K023, and K093 (California, New Jersey, Louisiana, Pennsylvania, Illinois, Texas, and Puerto Rico) contain 8 of the 36 operating lightweight aggregate plants. Although Pennsylvania, Illinois, and Pureto Rico have no lightweight aggregate plants, Pennsylvania and Illinois are surrounded by states having one or more plants.

TABLE 4.5-2. SIC CODES AND GEOGRAPHIC DISTRIBUTION OF INDUSTRIES GENERATING HAZARDOUS WASTES DESTRUCTIBLE IN THE LIGHTWEIGHT AGGREGATE MANUFACTURING ROTARY KILN[1,19]

Waste category	SIC code of waste generating industry	Geographic location
K015	2865	Two plants (locations not known)
K023	2869	Richmond and El Sequendo, California; Kearney and Bridgeport, New Jersey; Baton Rouge, Louisiana; Bridgeville and Neville Island, Pennsylvania; Cicero and Millsdal, Illinois; Texas City, Texas
K093	2869	Illinois, Texas, New Jersey, Puerto Rico, and California

4.5.2.7 Environmental Factors--

Impact on air pollution control devices--Atmospheric emissions from a typical lightweight aggregate rotary kiln consist of particulates, SO_2, NO_x, and CO. The quantity of these emissions varies with the type of fuel in use. Unfortunately, emission factors for this process are not available. Generally either a wet scrubber or a fabric filter is used to control these emissions; the wet scrubber is more popular.[48,51]

Depending on the characteristics of the pollutant and the increase in pollutant loadings, the addition of hazardous wastes may necessitate some adjustment in the control equipment. Highly corrosive wastes such as HCl may have a detrimental effect on pollution control devices. When a corrosive waste is being thermally destroyed, a neutralizing step may be required before the exhaust gases reach the wet scrubber and glass filters may be required in the fabric filter.[51]

Chlorinated wastes can also increase particulate loadings. The amount of increase would depend upon the mineralogical constituency in the raw material. Although raw materials vary, most will contain some sodium, calcium, potassium, and silicon compounds.[55] These compounds may react with the chlorine to form volatile chlorides that will exit into the atmosphere with the exhaust gases.

A potential exists for trace quantities of incomplete combustion products to escape into the stack gases. In addition, any heavy metals in the waste fuel will volatilize and exit through the stack. One firm is now successfully destroying easily combustible waste fuels (such as solvents) in many of their lightweight aggregate kilns.[48] This firm has established strict limits on the percent chloride, solids, and ash content to avoid operational and environmental problems.

4.5.2.8 Institutional Factors--

Because of rising energy costs, the lightweight aggregate industry seems more than willing to accept and adapt to the use of waste fuels. The largest firm in the industry has already become active in this area.[48] The three most inhibiting factors toward using waste fuels are:

- Public concern
- Impact on process and environmental control equipment
- Environmental impact

The industry is very sensitive to maintaining good public relations and avoiding public concern over incinerating hazardous wastes. Many older plants that were once located well beyond the city limits have found residential suburban neighborhoods growing up around the perimeter of their facilities. This has increased their sensitivity to the use of waste fuels and the potential impact of an accidental spill.

4.6 LIME INDUSTRY

The production of lime involves quarrying the raw limestone, preparing it by crushing and sizing, and calcining it to produce quicklime (CaO), which may be processed further by hydration. During calcination, the limestone is subjected to high temperatures that cause it to decompose. This process produces quicklime and releases CO_2. This reaction can be represented as:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$$

Quicklime can be manufactured in a variety of kilns: the long rotary kiln, the short rotary kiln with an external stone preheater, the vertical or shaft rotary kiln, the Calcinatic or rotary hearth kiln, and the fluidized-bed kiln. Rotary kilns, however, account for approximately 90 percent of the domestic lime production.[56]

According to the Bureau of Mines, U.S. Department of the Interior, lime producers at 153 plants in the United States and Puerto Rico sold or used 16,400 Gg (18.1 million tons) of lime in 1980.[57] The leading lime-producing states were Ohio, Pennsylvania, Missouri, Texas, and Alabama; together these states accounted for 48 percent of the total domestic output.

4.6.1 Process Descriptions

4.6.1.1 Rotary Kilns--

This manufacturing process involves the calcination of limestone at temperatures of approximately 1260°C (2300°F) in either a long rotary kiln or a short rotary kiln with an external stone preheater. Figure 4.6-1 presents a process flow diagram of a modern rotary kiln and hydration plant.

The major difference between the long kiln and the short rotary (other than dimensions) is that the short kiln is preceded by an external stone preheater, which increases productivity and decreases energy requirements. Hot exhaust air exiting the kiln exchanges heat with the limestone in an external preheater.

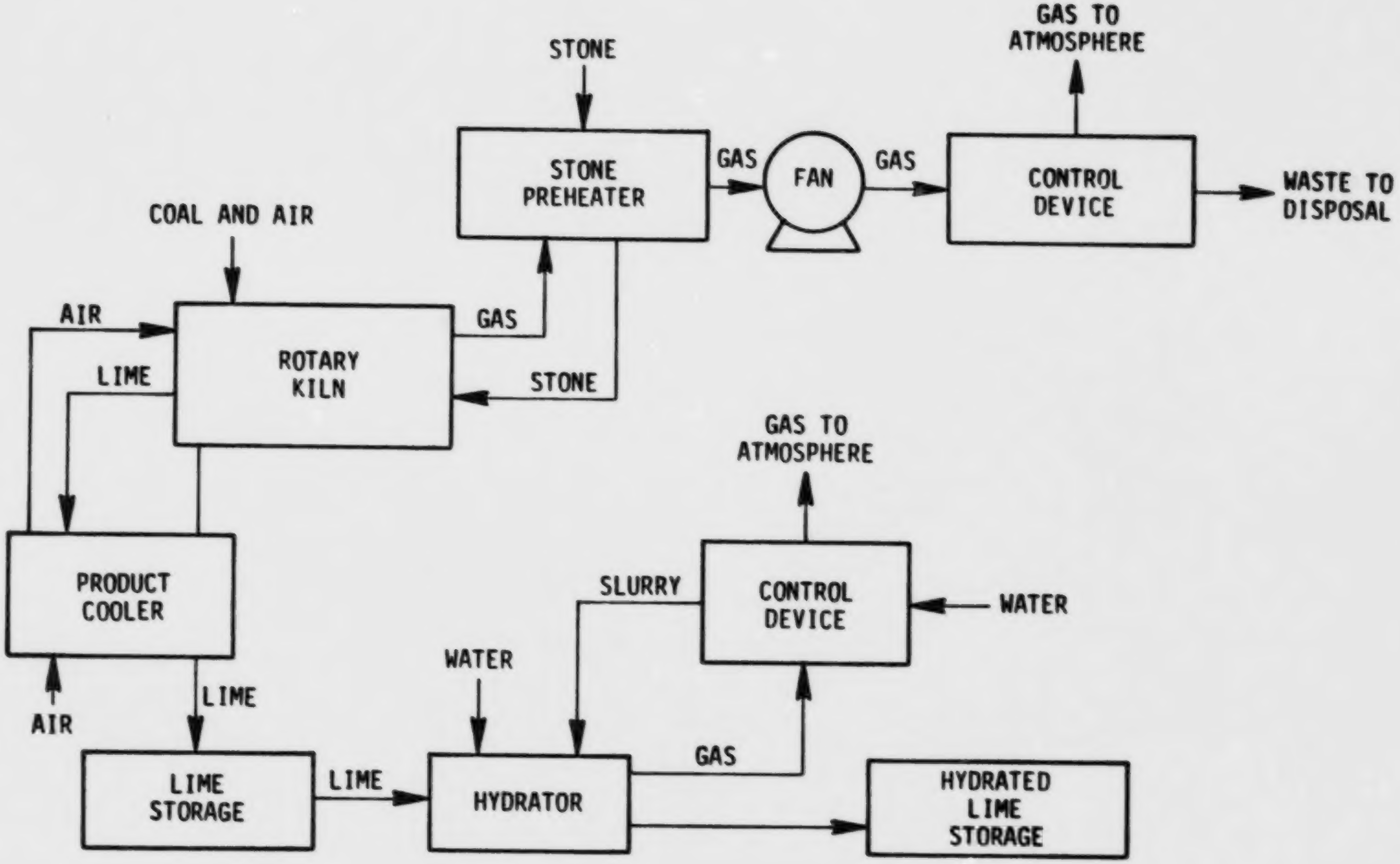

STONE
GAS TO ATMOSPHERE
STONE PREHEATER
GAS
FAN
GAS
CONTROL DEVICE
WASTE TO DISPOSAL
COAL AND AIR
AIR
GAS
ROTARY KILN
LIME
STONE
GAS TO ATMOSPHERE
PRODUCT COOLER
SLURRY
CONTROL DEVICE
WATER
WATER
AIR
LIME
GAS
LIME STORAGE
LIME
HYDRATOR
HYDRATED LIME STORAGE

Figure 4.6-1. Flowsheet for modern lime calcination and hydration plant.[56]

Both the long and short rotary kilns operate in similar fashion. The kilns are made of heavy steel plate lined with approximately 15 to 24 cm of refractory brick.[58] Although most rotary kilns are fired with pulverized coal, they can be adapted to firing natural gas or oil. The kilns vary in size from about 3 to 6 meters (10 to 20 feet) in diameter and 46 to 150 meters (150 to 500 feet) in length.[59] The kilns are installed at a 3- to 5-degree inclination on four or six foundation piers and revolve on trunnions at 1 to 2 rpm.[58] As shown in Figure 4.6-2, limestone is fed into the elevated end of the kiln and is discharged as quicklime into the cooler at the lower end. Approximately 10 percent of the kiln is filled with limestone or lime as the feed tumbles slowly and gently through the long cylindrical furnace. Cool air is usually introduced into the discharge end of the product cooler and subsequently into the kiln to serve as secondary combustion air.[58]

4.6.1.2 Vertical or Shaft Kilns--

Once the most widely used kiln in the United States, the total capacity of the vertical kiln has fallen well behind that of the rotary kiln. Basically, this kiln is an upright heavy steel cylinder lined with refractory material. Dimensions of the kiln may vary from 0.3 to 0.7 meter (0.9 to 2.4 feet) in diameter and 1.0 to 2.9 meters (3.4 to 9.4 feet) in height.[56] Vertical kilns of various design are in operation.

Most modern vertical kilns are divided into the following four generalized zones, often indistinguishable from each other:

1) Storage
2) Preheating
3) Calcining
4) Cooling

In the preheating zone, recirculated exhaust gases preheat the stone; in the calcining zone, 95 percent of lime burning occurs; and in the cooling zone, the incoming cool air, which flows upward countercurrent to the descending red-hot lime, cools the product and provides secondary combustion air for the calcining zone.[58]

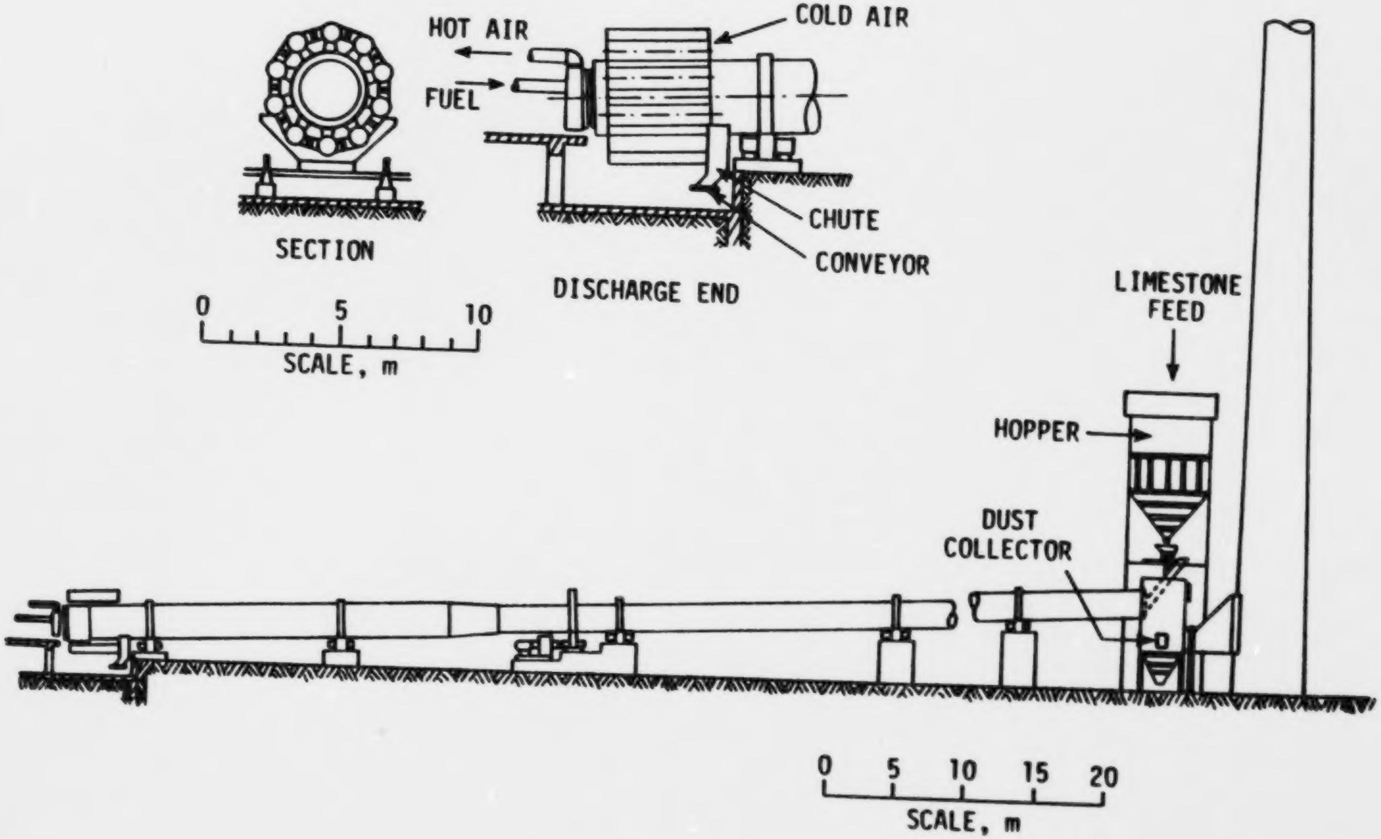

SECTION
HOT AIR
FUEL
COLD AIR
CHUTE
CONVEYOR
DISCHARGE END
0
5
10
SCALE, m
LIMESTONE FEED
HOPPER
DUST COLLECTOR
0
5
10
15
20
SCALE, m

Figure 4.6-2. Rotary kiln for processing lime.[58]

A higher average fuel efficiency is the primary advantage of the vertical kiln over rotary kilns. The primary disadvantages are its relatively low production rate and inability to burn solid fuel (coal) without degrading the quality of the lime.[56]

4.6.1.3 Calcimatic Kilns--

The Calcimatic (or rotary hearth) kiln is circular-shaped and has a slowly revolving doughnut-shaped hearth. The hearth is divided into zones, and precise temperatures are maintained in each of the different zones.[56] The quicklime product is discharged after it makes one revolution around the kiln. The heated gases from the calcination zone of the kiln are used to preheat the feed. The major disadvantage of this kiln is that it cannot be operated with solid fuel.

4.6.1.4 Fluidized-Bed Kilns--

Because of their specialized feed size requirements, the application of fluidized-bed systems has been limited in the domestic lime industry.[56] In this kiln, a very fine feed is fluidized by controlled air and combustion gases as it descends through the preheating and calcining zones. The finely divided limestone is physically agitated by turbulent air as it comes into direct contact with the combustion gases.

4.6.2 Process Assessment for Hazardous Waste Destruction

In this report only rotary kilns are considered as candidates for hazardous waste destruction. Because these kilns represent more than 90 percent of the domestic lime production, they appear to be a likely alternative for disposing of significant quantities of hazardous wastes. The other types of kilns were eliminated from further consideration for two reasons; the limited availability of process data and the relatively small number in operation.

4.6.2.1 Technical Factors--

Compatibility of hazardous wastes with process fuel--It appears feasible to inject hazardous wastes into rotary kilns along with the fuel (in most cases coal). Some retrofitting would be required to allow for the injection and subsequent atomization of liquid waste. This would entail the installation of a liquid burner/atomizer system, complete with the appropriate pump and piping. Appendix A provides a more detailed description of the appropriate equipment and procedures required for safe feeding and firing of hazardous waste.

Graphical determination of suitable waste categories--

Process data for the long rotary lime kiln--The temperature range [690° to 1890°C (1265° to 3440°F)] of a typical long rotary kiln indicates that destruction of hazardous wastes may be feasible. A typical long rotary kiln processes approximately 540 Mg (600 tons) of quicklime per day, has an average furnace volume of 720 m^3 (25,518 ft^3), and has an average volumetric flow rate of 910 Nm^3/min (34,560 scfm).[60]

Figure 4.6-3 plots the residence time for the mean- (Δt), and fast-path ($\Delta\bar{t}$) process curves for the long rotary lime kiln. These plots are overlaid on the hazardous waste curves to determine which hazardous waste categories are destructible in the kiln, given the time-temperature relationship. Based on data from this graph, Table 4.6-1 predicts the ability of a typical long rotary kiln to completely (99.99%) destroy the selected hazardous wastes. Since the average exit gas temperature of about 690°C (1265°F) falls below the lowest temperature in the graph (Figure 4.6-3), a conservative process line is not shown. Based on the extended case, it appears that the wastes in all the selected categories can be destroyed at the prevailing conditions in this kiln.

TABLE 4.6-1. APPLICABILITY OF THE SHORT AND LONG ROTARY LIME KILNS FOR THERMAL DESTRUCTION OF HAZARDOUS WASTES

K015	K023 K093	F003	K018, K025 K030	F004, F005, K022, K024 K027, K049, K094
Yes	Yes	Yes	Yes	Yes

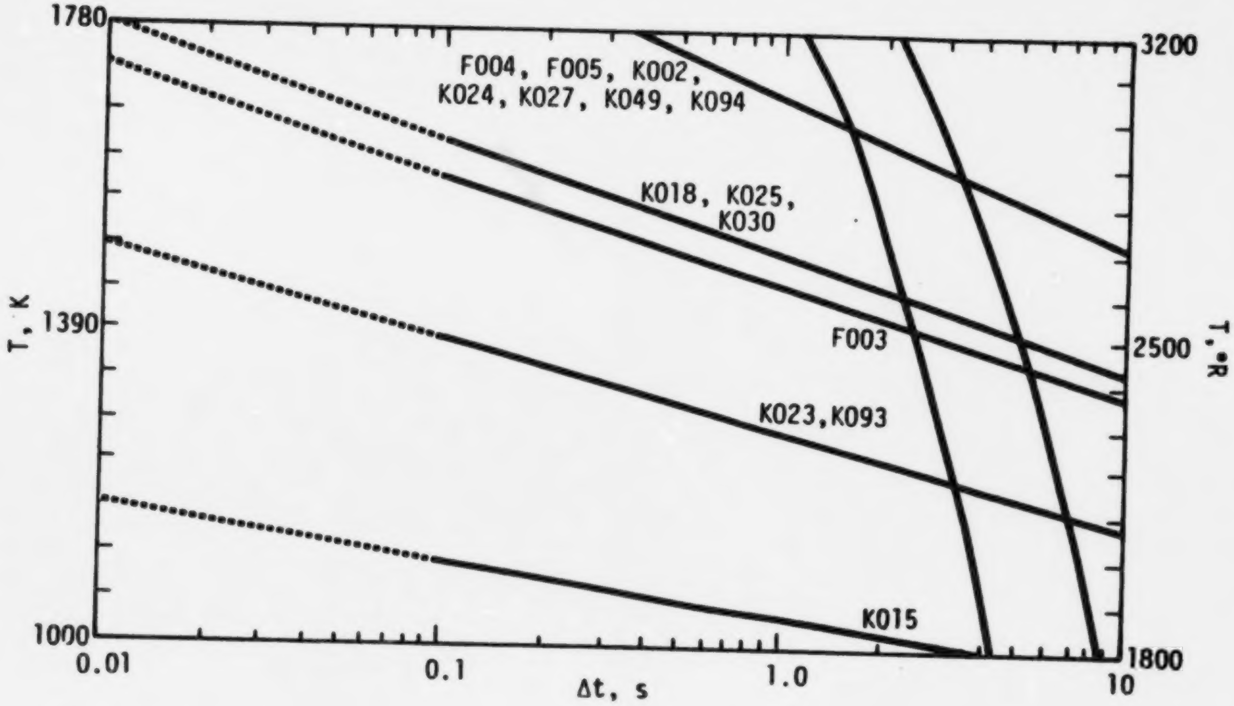


Figure 4.6-3. Hazardous waste destructibility in the long rotary lime kiln.

Process data for the short rotary kiln with an external stone preheater--The temperature range [1160° to 1840°C (2115° to 3340°F)] of a typical short rotary kiln with an external stone preheater suggests that thermal destruction of hazardous wastes in this kiln may be feasible. A typical short rotary kiln processes 540 Mg (600 tons) of quicklime per day, and has an average furnace volume and volumetric flow rate of 470 m^3 (19,792 ft^3), and 700 Nm^3/min (26,460 scfm), respectively.[60]

The Figure 4.6-4 process curves for the short kiln are overlaid on the hazardous waste curves to determine which hazardous waste categories are destructible given the kiln's time-temperature relationship. Table 4.6-1 presents predictions regarding the ability of this kiln to destroy completely (99.99%) the selected hazardous wastes. In the most conservative case, only those waste categories falling below the conservative process line are shown as being applicable. In the extended case it appears that the wastes in all the selected categories are destructible given the kiln's time-temperature relationship.

Effects on product quality and product application--Limestone and lime are used either directly or indirectly in more industries than any other natural substance. Among the leading individual end uses of lime are in steel manufacturing, water purification, alkali production, paper and pulp manufacturing, and sewage treatment; together these uses account for approximately 63 percent of the total 1979 consumption.[61] Lime is also used in medicine, insecticides, sugar refining, plant and animal food, gas absorption, and as a raw material in the production of calcium salts.

Many end uses of lime, such as in steel making, require a high product quality. Therefore, precautions are taken to select limestone and other raw materials that are low in impurities.

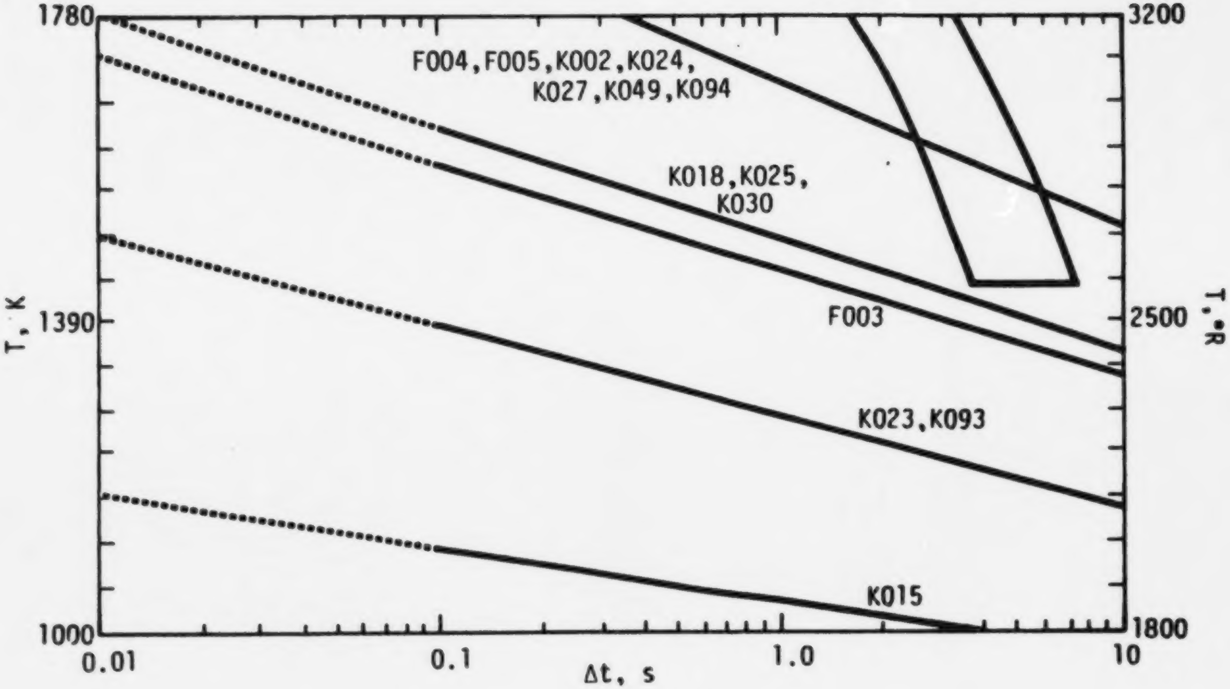


Figure 4.6-4. Hazardous waste destructibility in the short rotary lime kiln.

Impurities such as alumina, iron, and silica tend to combine chemically with lime and form aluminates, ferrites, and silicates.[58] The level of these impurities in the waste fuel must be minimal to ensure a high purity product. Chlorinated wastes are also likely to react with the calcium and form calcium chloride.[59] The boiling point of calcium chloride is 760°C (1400°F), whereas the exit gas temperature in a lime kiln ranges from 260° to 760°C (500° to 1400°F). With this temperature range, some calcium chloride probably would precipitate in the kiln and be retained in the lime product as an impurity.

The coal is most likely to contain sulfur, and to some extent so will the waste fuels. Most of this sulfur will be converted to SO_2 during fuel combustion and calcination. The extent to which the SO_2 could interact with the lime product will depend on the chemical composition of the stone, the temperature in the kiln, and the amount of excess oxygen in the kiln.[56] Studies have shown that most of the sulfur impurities in the lime product originate in the limestone raw material.[56]

The actual behavior of waste fuels in a lime kiln has not been reported in literature, and the actual impact of hazardous wastes on lime quality must be known to determine the feasibility of thermally destroying hazardous wastes in these kilns.

Impact on process hardware--The formation of silicates from the use of waste fuels could have some adverse effects on the process hardware. Silicates could be incorporated into the lime kiln coatings and lead to the formation of rings in the kiln, which could eventually disrupt kiln operations.[59] Ring formation could also be caused by fuels with a high ash content.[62] Because hazardous wastes generally have a lower ash content than coal, the ash ring problem could be minimized by destroying hzardous wastes. Highly chlorinated wastes could cause a buildup and baking problem in the short rotary kiln's stone preheater.[60] The preheater may need to be retrofitted with a bypass duct to minimize this problem.

In addition, the presence of trace quantities of metals and the formation of acids (such as HCl) could cause corrosion in the ducting and possibly interfere with the operation of air pollution control equipment. Highly corrosive wastes could also have a deleterious effect on the refractory lining of the kilns,[63] and excessive wear and tear of the refractories could increase kiln downtime for repairs.

Acceptable amounts of hazardous waste feed--According to industry experts, one-third megagram of coal with a heating value of 30 MJ/kg is required to produce one megagram of lime.[64] Based on this estimate and the assumption that 10 percent of the required heat input into the kiln can be provided by hazardous waste fuels, heat input through hazardous wastes is:

0.1 x 0.33 Mg coal/Mg lime x 30,000 MJ/Mg coal
= 990 MJ/Mg lime

For the most conservative case, the short rotary kiln is capable of thermally destroying only a few hazardous wastes.

By using an average heating value of 23,000 MJ/Mg, the quantity of hazardous waste feed can be estimated as 43 kg hazardous waste per Mg lime (86 lb/ton).

The typical lime kiln processes 540 Mg (600 tons) per day; therefore, up to 23.2 Mg (51,000 pounds) of waste fuel could be disposed of per day (based on the most conservative case for the short kilns). Assuming 260 days per year of operation, the annual disposal rate is estimated to be 6000 Mg/yr (6600 tons/yr).

In the extended case, both the long and short rotary kilns are shown to be capable of thermally destroying all of the selected hazardous wastes. Based on an average waste fuel heating value of 22 MJ/kg (9,400 Btu/lb), the quantity of waste feed for the extended case is estimated to be 45 kg waste/Mg lime (90 lb/ton).

For a typical lime kiln process rate of 600 tons per day (assuming 260 days of operation per year), the annual hazardous waste disposal rate is estimated to be 7000 Mg/yr (7700 tons/yr).

Trends in process fuel consumption--The rising cost of oil and natural gas over the last several decades has caused the domestic lime industry to use coal as their main fuel source, which necessitated the choice of the rotary kiln. Approximately 69.6 percent of all domestic lime kilns now burn coal and coke, an increase of 147 percent over 1972 usage.[65]

4.6.2.2 Geographical Matching of Industry Locations and Waste Generators--

Figure 4.6-5 shows the distribution of operating domestic lime plants by state. As mentioned earlier, Ohio, Pennsylvania, Missouri, Texas, and Alabama account for 48 percent of the total domestic lime production.[57]

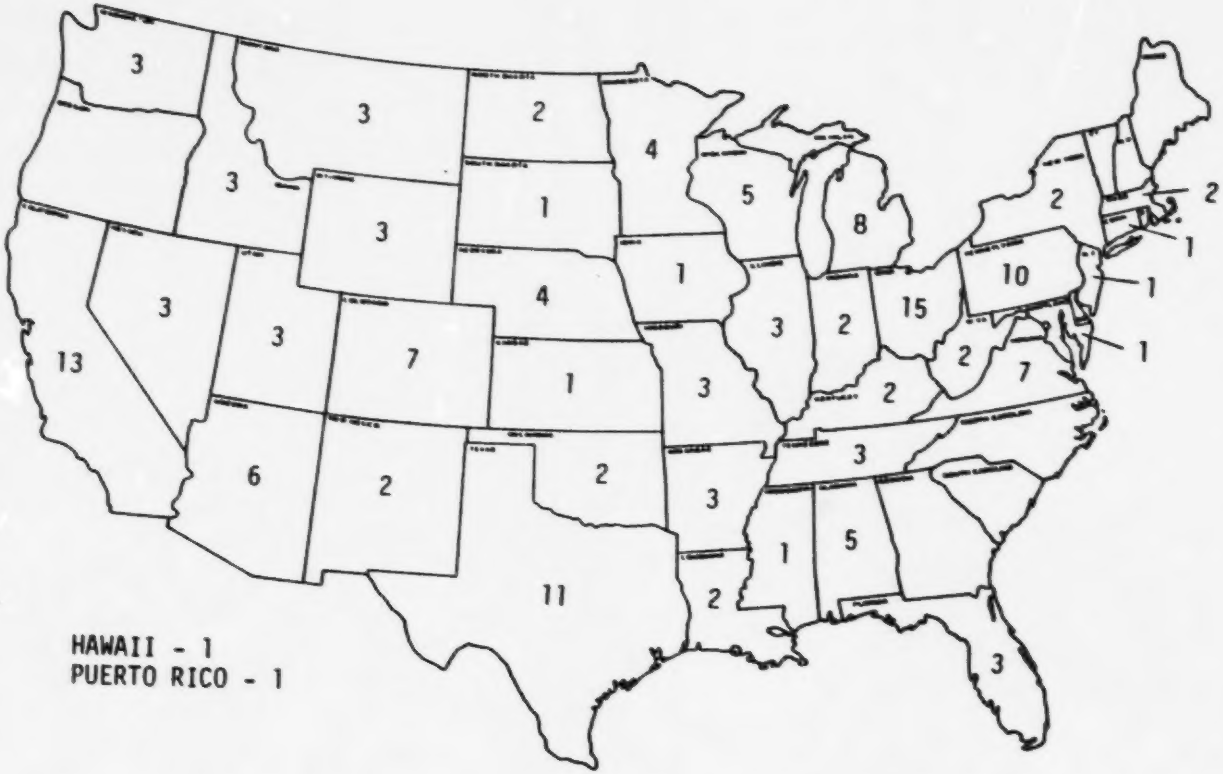
Table 4.6-2 presents the SIC code for each waste category and the waste's geographic distribution. Appendix B presents data concerning the annual generation rate in each waste category. In the short kiln's most conservative case, only the wastes in categories K015, K023, K093, and F003 are destructible. The areas where these wastes are generated (California, Illinois, Louisiana, New Jersey, Pennsylvania, Puerto Rico, and Texas) contain 41 of the 155 operating lime plants.

In the extended case, both the long and short rotary kilns are able to destroy all selected hazardous wastes. The areas specifically identified as generating these wastes (California, Illinois, Kansas, Kentucky, Louisiana, New Jersey, Ohio, Oklahoma, Pennsylvania, Puerto Rico, Texas, and West Virginia) contain 63 of the 155 operating lime plants.

The table shows that the sources of some wastes are widespread, although specific states are not mentioned. Such widespread geographical distribution greatly enhances the possibility of destroying these hazardous wastes in lime kilns.

4.6.2.3 Environmental Factors--

Impact on air pollution control devices--Atmospheric emissions from a typical rotary kiln consist of particulates, SO_2,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PUERTO RICO - 1

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Figure 4.6-5. Distribution of domestic lime plants, by state.[61]

TABLE 4.6-2. SIC CODES AND GEOGRAPHIC DISTRIBUTION OF INDUSTRIES THAT GENERATE HAZARDOUS WASTES DESTRUCTIBLE IN SHORT AND LONG LIME KILNS[1,19]

Waste category	SIC code	Geographic location
F003		Widespread
F004		Widespread
F005		Widespread
K015		Two plants (locations not known)
K018	2869	Houston and Freeport, Texas; Lake Charles and Baton Rouge, Louisiana; Deepwater, New Jersey; Long Beach, California
K022	2869	Widespread
K023	2869	Richmond and El Sequendo, California; Kearney and Bridgeport, New Jersey; Baton Rouge, Louisiana; Bridgeville and Neville Island, Pennsylvania; Cicero and Millsdale, Illinois; Texas City, Texas
K024	2869	Richmond and El Sequendo, California; Kearney and Bridgeport, New Jersey; Baton Rouge, Louisiana; Bridgeville and Neville Island, Pennsylvania; Cicero and Millsdale, Illinois; Texas City, Texas
K025	2865	Bound Brook, New Jersey; Pas and Willow Islands, West Virginia; Beaumont, Texas; Gibbstown, New Jersey; Geismar, Louisiana; New Martinville, West Virginia
K027	2869	Moundsville and New Martinsville, West Virgnina; Geismar and Lake Charles, Louisiana; Freeport and Baytown, Texas; Astabula, Ohio
K030	2869	Freeport, Deer Park, and Corpus Christi, Texas; Baton Rouge, Lake Charles, and Plaquemine, Louisiana; Pittsburg, California; Louisville, Kentucky; Wichita, Kansas
K049	2911	Widespread
K093	2869	Illinois, Texas, New Jersey, Puerto Rico, California
K094	2869	Illinois, Texas, New Jersey, Puerto Rico, California

NO_x, and CO. The industries use a wide variety of air pollution control equipment. Generally, primary particulate control is accomplished by multiple cyclones, which entrap 85 to 93 percent of the dust loading from rotary kiln systems.[58] A secondary system is required to abate most of the remaining dust. Among the secondary systems used, 45 percent are fabric filters, 40 percent are high-energy wet scrubbers, 10 percent are electrostatic precipitators, and 5 percent are gravel-bed filters and miscellaneous control equipment.[58] Table 4.6-3 shows the emission factors for a hypothetical 450-Mg (500-ton) per day rotary kiln plant that uses coal as its fuel and applies various control equipment. Solid waste quantities emitted from control devices are estimated to be 3200 kg/h at this hypothetical rotary kiln plant.[56]

If chlorinated wastes are burned, a corrosion-resistant scrubbing system would be required to capture the gaseous pollutants. Some plants now equipped with scrubbing systems may opt to burn only those wastes having a low chlorine content rather than retrofitting the plant to handle highly corrosive wastes.

A potential exists for trace quantities of incomplete combustion products such as organic chlorides to escape into the stack gases. The formation of such chlorinated acids should be avoided because of the possibility of the formation of calcium chloride. The actual behavior of the hazardous wastes and products of incomplete combustion will need to be investigated further by conducting a test burn to determine details of their environmental impact.

Fugitive emissions from the production of lime and the thermal destruction of waste fuels will occur primarily from transfer points, screening operations, hazardous waste pumps and piping, and loading and unloading operations.[56,59] Proper plant design and layout (e.g., by minimizing the height and number of drop points, enclosing elevators and screens, and installing packed seals on pumps) will greatly reduce these emissions. The installation of hoods over exit sources and the establishment of

TABLE 4.6-3. ROTARY KILN EMISSION FACTORS[56]

	Particulate, kg/Mg (lb/ton)	SO_2, kg/Mg (lb/ton)		Electrical energy factors, kWh/ton (Mg/ton) stone
		Low-sulfur coal	High-sulfur coal	
Uncontrolled (cyclone only)	17 (34.1)	-	-	18 (16[a])
Fabric filter	0.15 (0.3)	0.5 (1.0)	1.0 (2.0)	2.7 (2.42)
High-energy ESP	0.15 (0.3)	-	-	3.5 (3.19)
Low-energy ESP	0.25 (0.5)	-	-	2.4 (2.21)
Water scrubber (22 in. H_2O)	0.15 (0.3)	0.005 (0.1)	0.005 (0.1)	16.8 (15.2)
Water scrubber (15 in. H_2O)	0.25 (0.5)	0.005 (0.1)	0.005 (0.1)	11.9 (10.8)
Water scrubber (9 in. H_2O)	0.5 (1.0)	0.005 (0.1)	0.005 (0.1)	7.1 (6.45)
Gravel-bed filter	0.5 (1.0)	-	-	-

[a] Electrical energy required for kiln and associated equipment.

good housekeeping procedures could reduce fugitive emissions even further. These preventive measures need to be taken to ensure the safe incineration of hazardous wastes.

4.6.2.4 Institutional Factors--

Immediate industrywide acceptance of the idea of incinerating hazardous wastes in lime kilns is not likely. Such acceptance will be based on the costs associated with retrofitting a plant to accept hazardous waste, on public attitude, and on the savings associated with burning a relatively inexpensive fuel. The potential fuel savings may provide the incentive for industry to adapt to using hazardous wastes. The incinerability of the wastes and the impact on both the plant operation and the environment will have to be determined. The three major problems that may discourage the industry's use of waste fuels are the impact on product quality, the possible formation of kiln rings, and the impact on the external stone preheater (applies only to short kilns).

4.7 PRIMARY COPPER INDUSTRY

The high-temperature processes in the copper smelting industry are as follows:

Process	Process temperature, °C (°F)
Multiple-hearth roasting	760 (1400) at the bottom to 200 (400) at the top
Fluidized-bed roasting	650 to 760 (1200 to 1400)
Reverberatory smelting	980 to 1320 (1800 to 2400)
Flash smelting	1090 (2000)
Noranda furnace	1210 to 1320 (2200 to 2400)
Peirce-Smith converters	1180 to 1210 (2150 to 2200)
Hoboken converter	1200 (2200)
Electric smelting	980 to 1320 (1800 to 2400)

Figure 4.7-1 presents a generalized process flow diagram of the pyrometallurgical copper industry.

The following subsections describe each process and present an assessment of its potential for hazardous wastes incineration. Also presented is the rationale for eliminating most of the processes from further consideration.

4.7.1 Process Descriptions

4.7.1.1 Multiple Hearth Roasting--

The copper content of as-mined copper ores ranges from 0.5 to 2 percent, but usually runs less than 1 percent. Most copper ores are sulfide ores, which are concentrated by froth flotation. The concentrates contain copper (20 to 50%), sulfur (30 to 38%), iron (20 to 30%), and smaller amounts of various other metals. The purpose of roasting is to decrease the sulfur content by partial oxidation of the copper sulfide concentrates with air. Roasting also removes the water from the concentrates; volatilizes much of the arsenic (As), some of the antimony (Sb), and other elements in the feed; and preheats the concentrate before it is charged as calcined feed to the reverberatory furnaces.

In the multiple-hearth roaster, the concentrates are introduced into the top of a cylindrical vessel fitted with a series of round horizontal trays or hearths. As the concentrates are raked across each hearth they fall onto the next lower hearth and are subsequently discharged from the bottom of the roaster. The long retention time of the solids in the roaster results in an intimate contact between hot gases and solids. The bottom hearth temperature is around 760°C (1400°F). A limited amount of air is admitted into the roaster, along with sufficient fuel to maintain an adequate temperature. The varying fuel requirement depends on the sulfide content of the concentrates. The burning of sulfur to SO_2 is exothermic and releases heat. If the heat is sufficient to sustain the required temperature, the process is known as autogenous roasting.

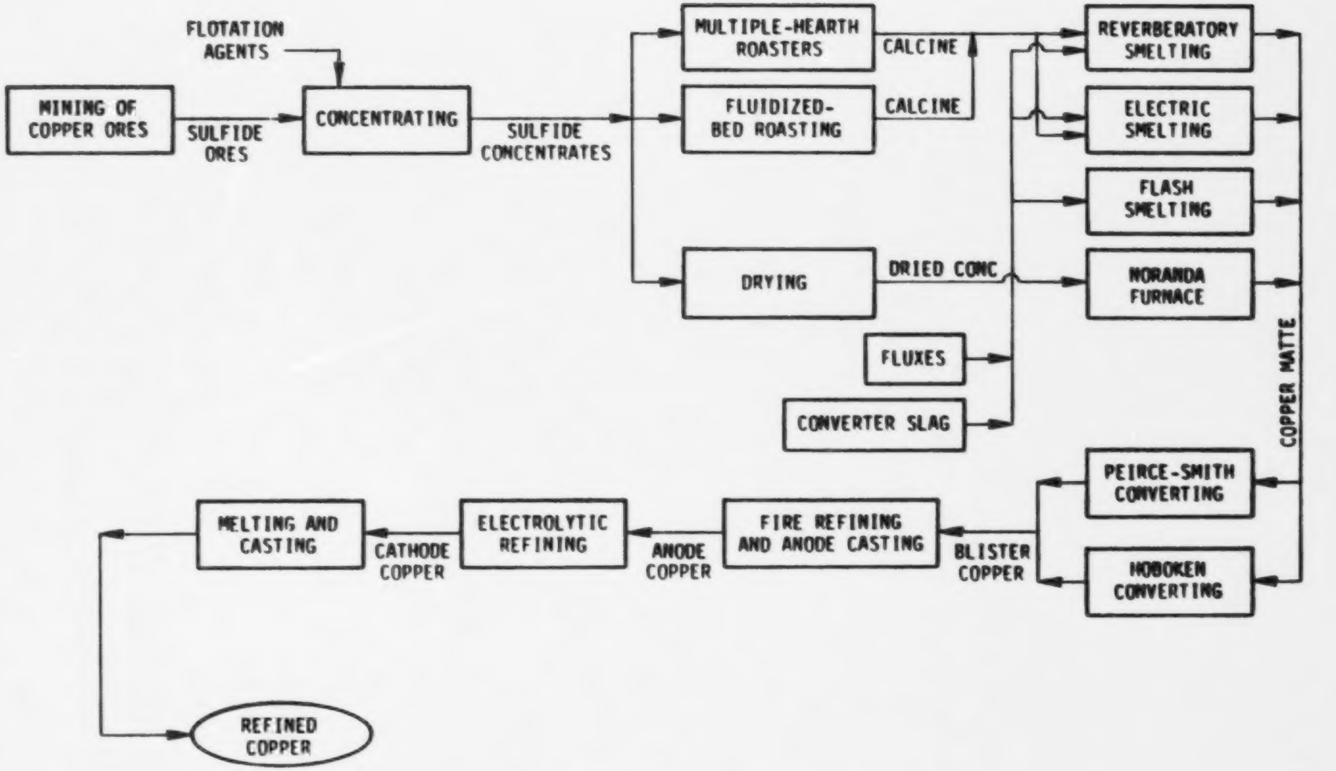
FLOTATION AGENTS
MINING OF COPPER ORES
SULFIDE ORES
CONCENTRATING
SULFIDE CONCENTRATES
MULTIPLE-HEARTH ROASTERS
FLUIDIZED-BED ROASTING
DRYING
CALCINE
CALCINE
DRIED CONC
FLUXES
CONVERTER SLAG
REVERBERATORY SMELTING
ELECTRIC SMELTING
FLASH SMELTING
NORANDA FURNACE
COPPER MATTE
PEIRCE-SMITH CONVERTING
HOBOKEN CONVERTING
BLISTER COPPER
FIRE REFINING AND ANODE CASTING
ANODE COPPER
ELECTROLYTIC REFINING
CATHODE COPPER
MELTING AND CASTING
REFINED COPPER

Figure 4.7-1. Simplified flow diagram of the primary pyrometallurgical copper process.[69]

Only four plants in the U.S. primary copper industry use multiple-hearth roasters. Three of these plants are in Arizona (at Hayden, Douglas, and Tacoma), and one is in El Paso, Texas. The highest temperature achieved in roasting is 760°C (1400°F). No new multiple-hearth roasters have been installed in recent years; all new roasters since 1960 have been fluidized-bed units.[68] Those multiple-hearth furnaces still in operation usually generate large amounts of fugitive emissions and are poorly controlled. This process is not considered further for destroying hazardous wastes because its relatively low operating temperature, fugitive emission potential, and the small number of operating units make it a poor candidate.

4.7.1.2 Fluidized-Bed Roasting--

The function of fluidized-bed roasting is the same as that of multiple-hearth roasting. In this process, the gas is a recycled stream of flue gas, into which regulated streams of air (no excess air) and fuel gas are introduced. The copper concentrate solids are continuously fed and the smaller roasted concentrate particles are collected with cyclones after they are carried out of the fluidized-bed area with the exhaust gases, and the larger concentrate particles are collected as they overflow the fluid bed portion of the vessel. The temperature of the bed is around 650° to 760°C (1200° to 1400°F). Intimate contact between solid particles and gases is achieved through the constant agitation of the fluidized-bed. Any chemical reaction that takes place in the fluidized-bed roaster between the solids and the gas happens very quickly, with no cold pockets or hot spots. Both the fuel and the oxygen are completely consumed, and because there is no excess air, the SO_2 content of the flue gas stream is high (12 to 16 percent of the exhaust). This high SO_2 content is beneficial for the production of sulfuric acid, elemental sulfur, or liquid SO_2.

Only four plants in the United States have fluidized-bed roasters. These plants are located at Hayden, Arizona; Morenci, Arizona; Anaconda, Montana (currently shut down); and Copperhill, Tennessee. Although specific matching of certain waste suppliers and smelters might be arranged, the locations and limited number of these plants rule out widespread national application.

The fluidized-bed roaster process is eliminated from further consideration for hazardous waste disposal because of the limited number of facilities and the relatively low process temperature.

4.7.1.3 Reverberatory Furnace Smelting--

The reverberatory furnace is the most widely used unit for matte smelting. Matte smelting produces separable liquid phases of slag and a copper-rich sulfide phase (matte) by the melting of concentrates or roaster calcines. The smelting is done in a arch-roofed horizontal hearth furnace at 980° to 1320°C (1800° to 2400°F). The slag is discarded if the copper content is below 1 percent. Reverberatory furnaces use large quantities of hydrocarbon fuels. Reverberatory furnaces are used extensively because of their versatility; all types of material (lumpy, fine, wet, or dry) are readily smelted in a continuous operation.

The heat for smelting and for maintaining the temperatures of the liquid slag and matte is provided by combustion of oil, natural gas, or coal in burners situated at one end of the furnace. The flame and hot combustion gases travel the entire length of the furnace and achieve an efficient heat transfer with the solid charge and molten pool of slag and matte. Based on the time/temperature profiles inside the furnace, it is possible to consider the incineration of hazardous liquid wastes in this process.

4.7.1.4 Peirce-Smith Converters--

The molten matte is transported from smelting and charged directly into the Peirce-Smith converter along with flux. This converter is a horizontal cylindrical vessel that blows compressed air into the molten matte layer via tuyeres along the longitudinal length of the vessel. The purpose of converting is to remove iron, sulfur, and other impurities from matte; this produces a liquid metallic copper known as crude blister copper (98.5 to 99.5% Cu) and slag.[69] This is achieved by oxidizing the molten matte at a high temperature [1180° to 1210°C (2150° to 2200°F)]. The two products occur at different stages of the process. The slag is removed first, and then the blister copper. They are poured separately from the converter mouth by rotating the converter about its longitudinal axis. The converting process produces hot SO_2-laden gases, which are collected by means of a fixed hood above the converter. The gases, which contain 2 to 6 percent SO_2, usually pass through a waste heat boiler and an electrostatic precipitator for particulate control before being sent to an acid plant for recovery of SO_2 as sulfuric acid. The converting reactions are exothermic and the process is autogenous.

Peirce-Smith converters generate considerable quantities of fugitive dust, fumes, and SO_2. Whenever flux is added or copper and slag are to be poured out of the mouth of the converter, the converter has to be tilted away from the collection hood, which is when most of the fugitive emissions occur. These emissions, which occur between the hood and converter mouth during blowdown, are minimized by placing the hood as close as possible to the converter mouth. Because of the high fugitive emissions and the lack of a proper method for charging of hazardous wastes (i.e., matte is poured from ladles), the Peirce-Smith converter is considered unsuitable for hazardous waste incineration.

4.7.1.5 Hoboken Converter--

The Hoboken converter is another type of furnace used to produce crude blister copper from the matte formed in the smelting process. Its function is identical to that of the Peirce-Smith converter. The principal difference is that the flue that removes the gas from the converter is an integral part of the converter construction rather than a hood mounted above it. This design minimizes infiltration of air, minimizes local losses of

SO_2 from the converter mouth, and allows production of a gas with a higher and more uniform SO_2 content. The main operating advantages are minimal fugitive emissions during charging of molten matte, tapping, and slagging.

The furnace operates at around 1210°C (2200°F) and at atmospheric pressure. The SO_2 generation is intermittent, but a battery of several converters will produce a stream of SO_2 of sufficient concentration and flow to allow production of sulfuric acid. The converter gases pass through cyclones and an electrostatic precipitator before finally arriving at the acid plant. Only one plant (in Inspiration, Arizona) uses the Hoboken converter. This plant has five, only four of which operate at any given time.

Because there is only one U.S. plant that uses Hoboken converters and there is no proper method for charging hazardous wastes into these converters (i.e., matte is poured into the furnace from ladles and there are no burners), this process has been eliminated from further consideration for the destruction of hazardous wastes.

4.7.1.6 Noranda Furnace--

The Noranda furnace is a continuous smelter. In theory, this design is a single furnace that combines most of the functions of roasting, smelting, and converting. This process approaches a one-step method of producing copper metal from ore concentrates. Only one plant in the United States (in Garfield, Utah) operates Noranda furnaces. The Noranda furnace is a horizontal cylinder about 21 meters (70 feet) long, into which a mixture of concentrate and flux is continuously fed, along with fuel and oxygen. The furnace is fired from both end walls. The mixture reacts to form blister copper, matte, and slag, which separate into layers. Additional oxygen-enriched air is blown through side-mounted tuyeres into the matte layer to produce blister copper. Slag and blister copper are tapped intermittently from the furnace. The one U.S. facility produces a high-grade matte (70% copper), which is sent to a Peirce-Smith converter for the production of blister copper and the removal of most of the impurities that would be in the blister copper if it were made in the Noranda furnace directly. The operating temperature ranges from about 1210° to 1320°C (2200° to 2400°F). Particulate loads, which are dependent on the size distribution of the feed, are quite substantial. These particulates flow with the high-temperature exhaust gases through a connected waste heat boiler and are collected as the exhaust gas flows through hot cyclones and an ESP. The dust is either pelletized or directly recycled. The gas stream is cleaned and used for sulfuric acid production.

Because only one plant in the United States uses the Noranda furnace, this process is not considered further.

4.7.1.7 Flash Smelting--

In flash smelting, finely pulverized ore concentrates are injected into a combustion chamber along with ground flux and preheated air or oxygen. Part of the sulfur in the concentrates burns in a "flash" combustion as the particles travel through the chamber. The exothermic reactions taking place normally maintain the smelting temperature, but some concentrates may require additional fuel. External fuel is required during startup of the furnace. Matte and slag form into separate layers within the chamber, as in a reverberatory furnace. The matte is sent to the conventional converters for further processing into blister copper. The slag is further processed to recover any copper content.

Temperature in a flash chamber is maintained at approximately 1090°C (2000°F). Fuel consumption in the Outokumpu type is about two-thirds of that required by a reverberatory furnace of equal capacity. Except for startup and abnormal operations, fuel is required for preheating the combustion air. Flash smelting removes a large percentage of sulfur as SO_2 (50 to 80%).[69]

The gas stream leaving the flash smelter contains 10 to 20 percent SO_2 suitable for sulfuric acid manufacture.[69] Only one plant operating in the United States (in New Mexico) uses an Outokumpu flash smelting unit. This flash smelting plant has an acid manufacturing unit. Complete removal of particulates from the gas stream is achieved by the use of a waste heat boiler, cyclones, balloon flues, and electrostatic precipitators.

Because of the highly selective nature of the raw material feed and because there is only one U.S. flash smelting plant, this process was eliminated from further consideration for destroying hazardous wastes.

4.7.2 Detailed Evaluation of Reverberatory Furnace Smelting

4.7.2.1 Process Description--

Copper smelting is the process of removing iron and other impurities from a roasted or dried ore concentrate and producing a molten mixture that can be efficiently processed by a copper converter. This process is most often accomplished with a reverberatory furnace. Figure 4.7-2 shows a cross section of a typical reverberatory smelting unit. The term "reverberatory" refers to the configuration of the flame, which enters the chamber from one end, reverberates off the roof, and strikes the charge from above. As the charge melts, it separates into two layers: matte and slag. The matte consists of cuprous sulfide-ferrous sulfide (Cu_2S-FeS) (35 to 65% Cu).[68] The slag, which contains iron oxide, combines with silica flux to form silicates and other compounds of calcium, magnesium, and aluminum. Slag is drained periodically from a skimming bay at one end of the furnace; matte is withdrawn periodically through tap holes in the lower furnace wall at the other end of the furnace. Energy consumption in this process is about 3.5 to 7.6 GJ/Mg (3.0 to 6.5 million Btu/ton) of charge. Natural gas, pulverized coal, and oil are used as fuel. The temperature of the slag and matte during operation ranges from 1150° to 1250°C (2100° to 2300°F), and the gases leave the furnace 38° to 93°C (100 to 200°F) hotter than the slag.[68]

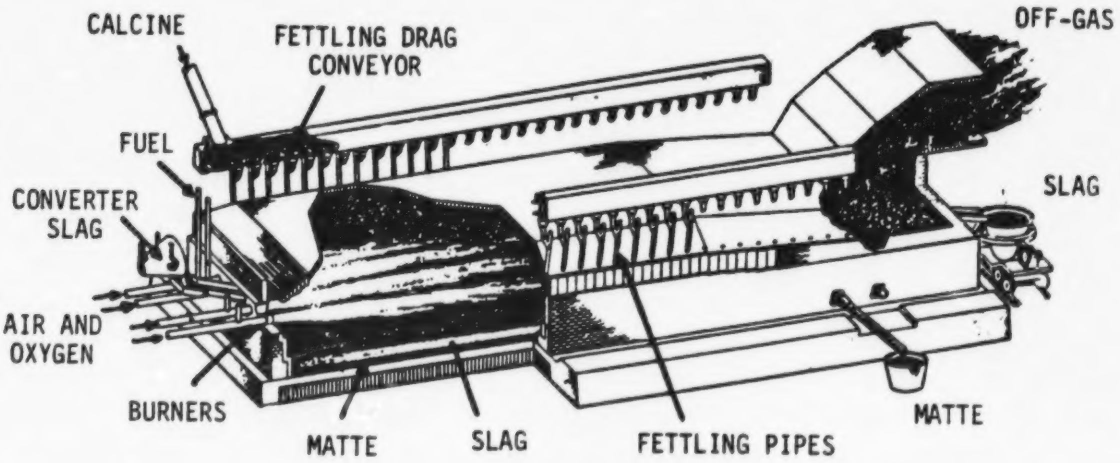
CALCINE
FETTLING DRAG CONVEYOR
OFF-GAS
FUEL
CONVERTER SLAG
SLAG
AIR AND OXYGEN
BURNERS
MATTE
SLAG
FETTLING PIPES
MATTE

Figure 4.7-2. Cross section of a reverberatory furnace.

Waste heat boilers are typically used to recover some of the heat in the exhaust gases.

A total of 11 plants in the U.S. primary copper industry use reverberatory furnaces. Table 4.7-1 lists the plants and number of furnaces at each. Figure 4.7-3 shows the geographical location of these plants; six are located in Arizona and one each in the states of Washington, Nevada, New Mexico, Texas, and Michigan.

TABLE 4.7-1. LIST OF REVERBERATORY FURNACE LOCATIONS IN THE U.S. PRIMARY COPPER INDUSTRY

Company	Location	No. of reverberatory furnaces
Asarco, Inc.	El Paso, Texas	1
	Hayden, Arizona	2
	Tacoma, Washington	2
Copper Range Company	White Pines, Michigan	2
Kennecott Copper Corp.	Hurley, New Mexico	2
	Hayden, Arizona	1
	McGill, Nevada	2
Magma Copper Co.	San Manuel, Arizona	3
Phelps Dodge Corp.	Morenci, Arizona	5
	Douglas, Arizona	2
	Ajo, Arizona	1

Two methods of hazardous waste destruction in a copper smelting furnace can be evaluated: 1) liquid wastes could be co-fired with the fuel, and 2) solid and semisolid hazardous wastes could be charged into the furnace. Because of the high potential for fugitive emissions from handling and conveying solid and semisolid hazardous wastes, this section addresses only the co-firing of liquid wastes and fuel.

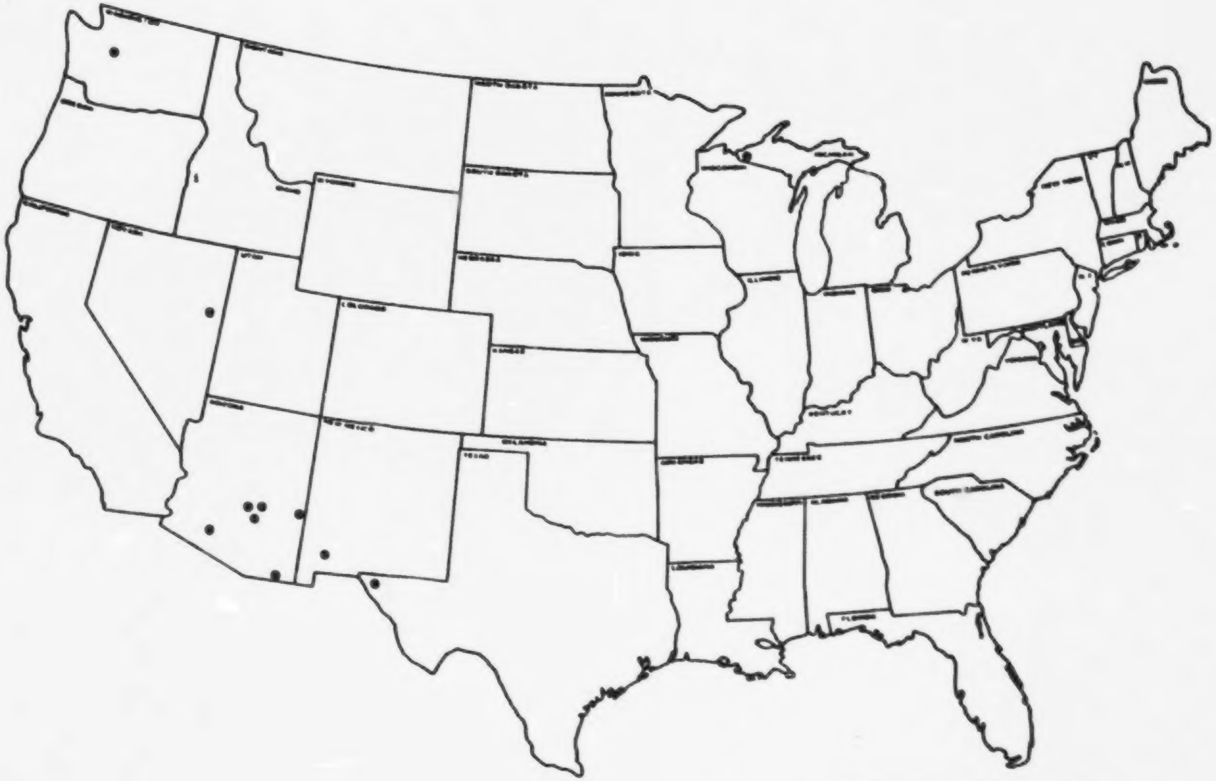Reproduced from
best available copy.

Figure 4.7-3. Distribution of reverberatory furnaces in the U.S. primary copper industry, by state.[69,70]

4.7.2.2 Technical Considerations--

Graphical determination of suitable waste categories--Pertinent process conditions for determining the time/temperature relationship in reverberatory copper smelting furnaces are:

Volume of furnace	566 m^3 (20,000 ft^3)
Gas volumetric flow rate	2630 Nm^3/min (100,000 scfm)
Maximum reaction zone temperature	1430°C (2600°F)
Exit gas temperature	1320°C (2400°F)

Figure 4.7-4 shows a gas temperature profile for a reverberatory furnace with and without oxygen enrichment of the air. Figure 4.7-5 presents a time/temperature curve for a typical reverberatory smelting furnace. The high furnace temperature and the gas retention time of about 2 seconds [as estimated by the process model (Section 3)] are suitable for the destruction of the hazardous wastes in several categories.

As Figure 4.7-5 shows, K-015, K-023, K-093, F-003, K-018, K-025, and K-030 wastes are projected to be 99.99 percent destroyed if used as part of the fuel in a reverberatory furnace.

Effects on product quality and product application--Table 4.7-2 indicates the distribution of elements between the matte and slag in a typical smelter. The matte contains most of the heavy metals present in the charge, practically all the gold and silver, and part of the arsenic and antimony. Any of these elements contained as impurities in the hazardous waste that might find their way into the slag or matte layers should not affect the quality of the matte or prevent the slag from being discarded in the normal manner. The products of combustion would be emitted with the flue gas, and no matte contamination is expected.

Major uses of copper are for electrical equipment and supplies, construction (plumbing, fixtures, and roofing), and industrial machinery. Any possible minor contamination is not expected to affect these applications.

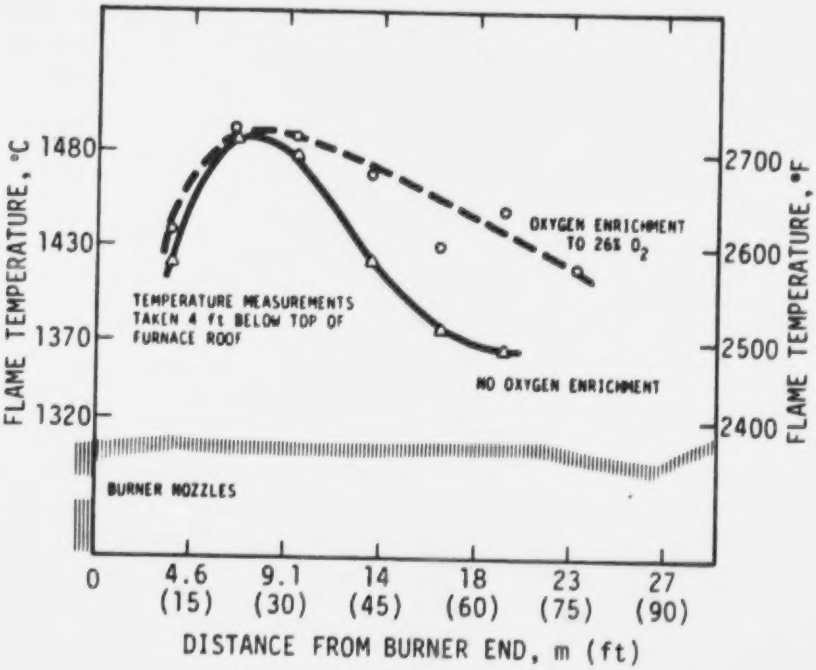

Figure 4.7-4. Temperature profile in a reverberatory furnace.

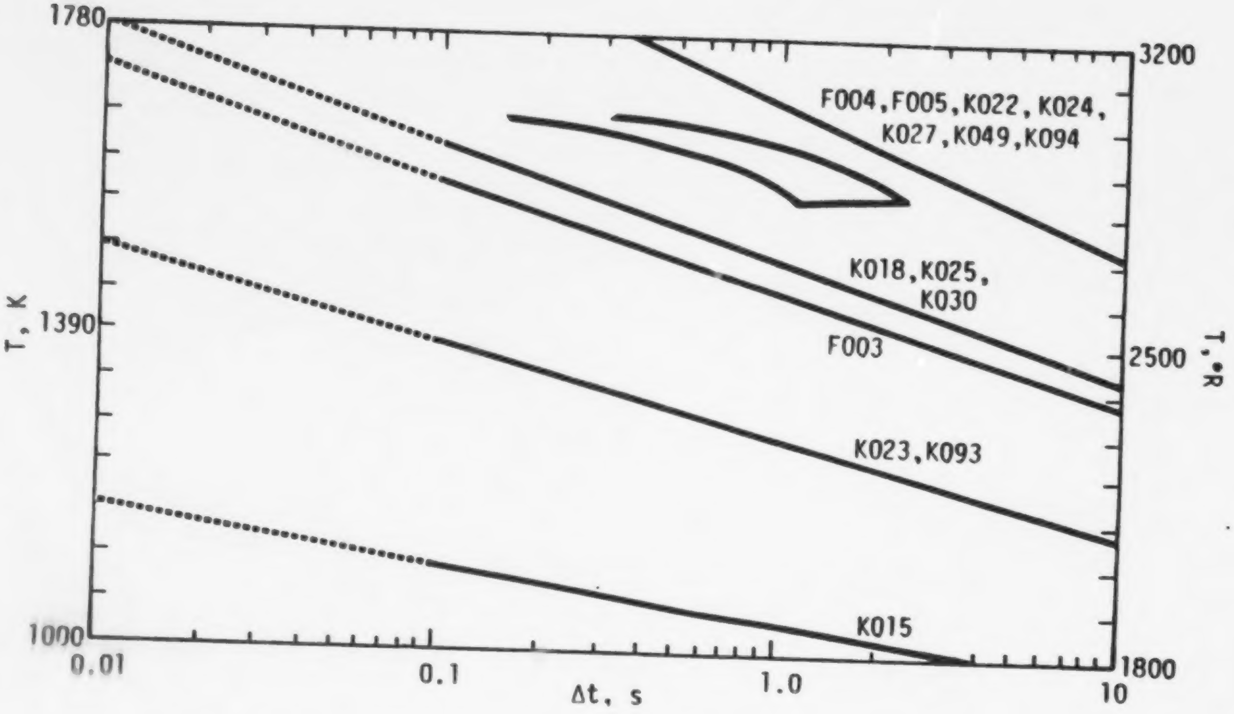

Figure 4.7-5. Hazardous waste destructibility predictions for reverberatory furnaces in primary copper smelting.

TABLE 4.7-2. DISTRIBUTION OF ELEMENTS DURING MATTE SMELTING[68]

Metal	Distribution		
	Matte	Slag	Volatilized[a]
Alkali and alkaline earth metals, aluminum, titanium		100	
Silver, gold, platinum metals	99	1	
Antimony	30	55	15
Arsenic	35	55	10
Bismuth	10	10	80
Cadmium	60	10	30
Cobalt	95	5	
Lead	30	10	60
Nickel	98	2	
Selenium	40		60
Tellurium	40		60
Tin	10	50	40
Zinc	40	50	10

[a] Not including solids blown from the furnace (dust losses).

Impact on process hardware--The refractory used in copper smelting reverberatory furnaces is typically either magnesite (MgO) or chrome magnesite ($Cr_2O_3 \cdot MgO$).[68] Halogenated wastes and wastes containing alkali metals should be avoided because they could drastically shorten the life of the refractory lining.

Acceptable amounts of hazardous waste feed--Fuel consumption in the reverberatory copper smelting furnace varies according to whether the charge is a wet or dry concentrate or calcine (from the roaster). A typical heating requirement is about 5.8 GJ/Mg (5 million Btu/ton) of charge. In a furnace processing 1360 Mg (1500 tons) of charge per day, this is equivalent to about 200 kl (52,000 gal) of oil per day. Assuming a substitution rate for hazardous waste fuel of 10 percent, about 18,900 liters/day (5000 gal/day) of waste could be disposed of per day or about 14 liters/Mg (3.3 gal/ton) of charge.

Provisions for waste introduction--Pulverized coal, oil, and natural gas are used as fuels for reverberatory furnaces. Wastes could be stored in a tank and metered into the pulverized coal or the oil before it reaches the burner. If cofired with natural gas, burner modifications at the furnace and separate lines from the waste storage tank to the furnace(s) would be necessary. The existing burners usually have low-pressure air and fuel delivery systems and are often equipped to handle many types of fuel. In these cases, burner modifications may not be necessary.

Projected trends in process fuel--Although pulverized coal was once the predominant fuel, oil and natural gas are now the most used fuels because they are easier to transport, store, and burn. Rapidly increasing prices of oil and natural gas, however, may cause a return to pulverized coal. Increased fuel costs are also causing a trend away from reverberatory furnace smelting toward other processes because this process does not make significant use of the energy available from oxidizing the sulfide charge.

4.7.2.3 Geographical Matching of Industry Locations and Waste Generators--

Figure 4.7-5 shows that hazardous wastes in categories K015, K023, K093, F003, K018, K025, and K030 should be 99.99 percent destroyed if used as part of the fuel in a reverberatory furnace. Categories K015, K018, and K030 wastes probably will not be compatible with furnace operation because they contain halogenated compounds. The K023, K093, and F003 wastes generated in Illinois and F003, K025, and K093 wastes generated in the Texas area are relatively close to smelter locations. The limited number of furnaces, however, rules out widespread national application.

Table 4.7-3 shows the liquid waste categories that can be destroyed in copper smelting reverberatory furnaces.

TABLE 4.7-3. APPLICABILITY OF COPPER SMELTING REVERBERATORY FURNACES FOR THERMAL DESTRUCTION OF HAZARDOUS WASTES

Types of wastes	Applicability	Remarks
K015	No	Highly chlorinated
K023	Yes	Except dichlorethane
K093	Yes	
F003	Yes	
K018	No	Highly chlorinated organics
K025	Yes	
K030	No	Chlorinated

4.7.2.4 Environmental Concerns--

Gases from the reverberatory furnace typically pass through a waste heat boiler and then through an electrostatic precipitator for particulate removal. The gases may pass through a spray chamber or balloon flues before entering the ESP units. The degree of particulate removal ranges from 50 to 99.99 percent.[69]

Fugitive emissions that occur during charging and tapping may be a problem when firing hazardous waste. Any residues remaining after hazardous waste destruction will pass into the control system or enter the metal or the slag. The ESP dust is usually recycled to the furnace, whereas the slag from the reverberatory furnace is usually landfilled on site. Heavy metal concentrations in the slag would have to be monitored closely.

4.7.2.5 Economic Factors--

Fuel costs are a large part of the reverberatory smelter operating costs. Fuel credits from high-Btu wastes may decrease the rate of copper smelter switchover from reverberatory smelters to more fuel-efficient smelting techniques.

4.7.2.6 Institutional Factors--

Reverberatory furnace smelters are not located in highly populated areas. Thus, the major obstacle for hazardous waste destruction will probably come from within the industry. The threat of reduced productivity and quality may preclude consideration of hazardous waste destruction in reverberatory copper smelters.

4.8 PRIMARY LEAD INDUSTRY

The United States leads the world in lead production, and accounted for about 15 percent of the total world mine production in 1978.[71] Figure 4.8-1 shows the locations of U.S. primary lead smelters and refineries. Three of the five U.S. lead smelters are located in southeastern Missouri's "New Lead Belt." More than 80 percent of the ore mined specifically for lead in the United States also comes from this region. Table 4.8-1 shows the capacities of the individual smelters/refineries.

4.8.1 Process Descriptions

Lead is usually found in nature as the sulfide ore, galena (PbS), which also contains small amounts of copper, iron, zinc, and other trace elements. It is generally processed at the mine,

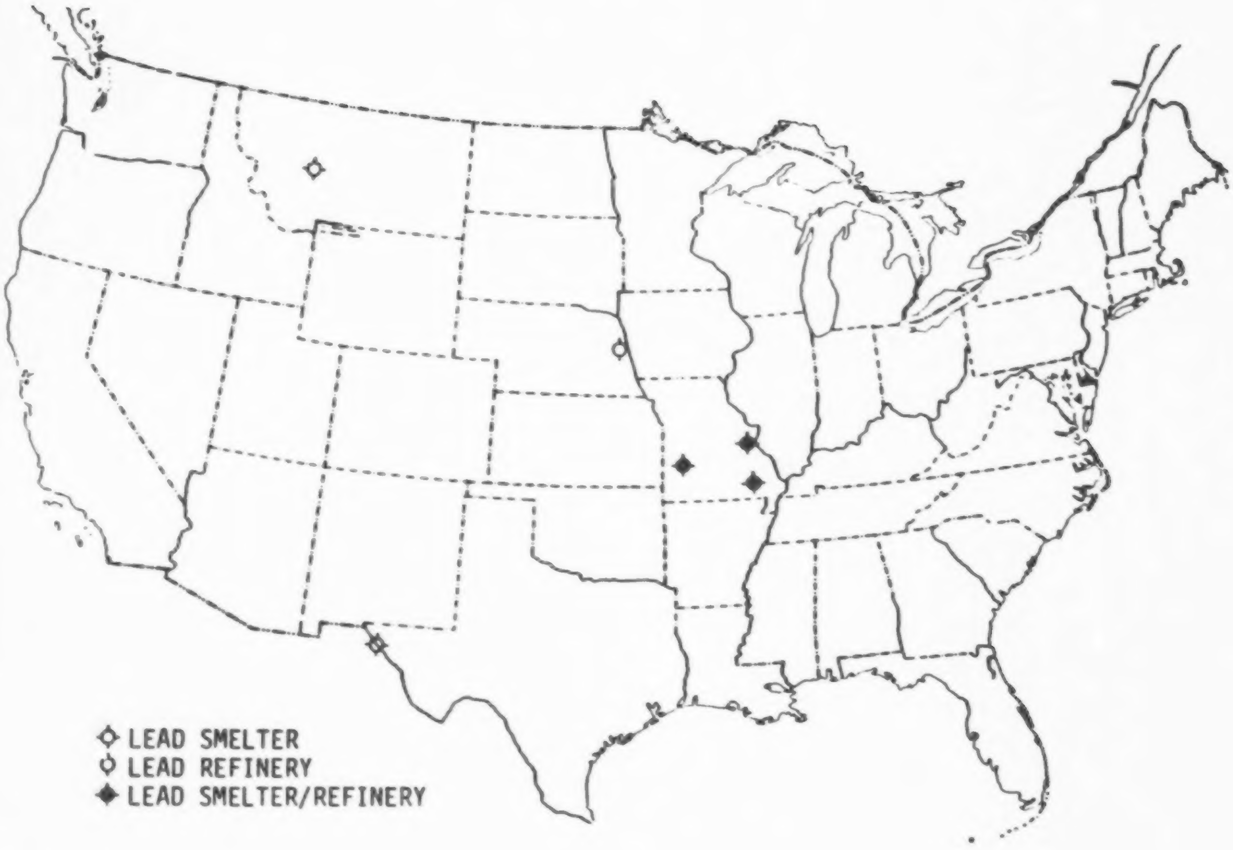
◇ LEAD SMELTER
○ LEAD REFINERY
◆ LEAD SMELTER/REFINERY

Figure 4.8-1. Distribution of primary U.S. lead smelting and refining facilities.[71]

TABLE 4.8-1. U.S. PRIMARY LEAD PRODUCERS[71]

Company	Location	Description	Design capacity, Mg/yr (tons/yr)
Amax-Homestake Lead Tollers	Boss, Missouri	Smelter/refinery[a]	127,000 (140,000)
Asarco, Inc.	East Helena, Montana	Smelter	109,000 (120,000)
	El Paso, Texas	Smelter	109,000 (120,000
	Glover, Missouri	Smelter/refinery[a]	99,300 (110,000)
	Omaha, Nebraska	Refinery	163,000 (180,000)
St. Joe Minerals Corporation	Herculaneum, Missouri	Smelter/refinery[a]	204,000 (225,000)

[a] The smelting and refining of Missouri lead ore takes place in the same plant.

from an ore of 3 to 8 percent lead to a concentrate of 55 to 70 percent lead. Lead content of some of the high-grade Missouri ores exceeds 70 percent even before the concentrating process.[71] Typically, 13 to 19 percent by weight of the concentrate is sulfur.[68]

The simplified flow sheet in Figure 4.8-2 shows the fundamental operations involved in the production of lead from lead sulfide concentrates. The primary lead industry uses various types of high-temperature furnaces (each of which has unique functions) in the process of recovering lead and other trace metals from the concentrates. A list of these furnaces, along with their primary functions, is presented below.[71]

1. Sintering furnace: Sintering (blending, pelletization and roasting) for subsequent operations.
2. Blast furnace: Reduction of sintered feed.
3. Slag fuming furnace: Recovery of metal values from blast furnace slag.
4. Drossing kettle: Initial step in lead refining.
5. Dross reverberatory furnace: Separation of components in dross.
6. Roasters: Recovery of cadmium from sinter dust.
7. Reverberatory softening furnace: Purification of drossed lead bullion.
8. Softening slag treatment furnace: Recovery of antimony from slag.
9. Faber-du-Faur type retorting furnace: Recovery of zinc.
10. Cupel furnace: Purification of retort metal.

The sintering machines, blast furnaces, and refining kettles are characteristic of all five domestic primary lead smelters, whereas the other types of furnaces are specific to certain individual smelters. Capacities of some of these other furnace types

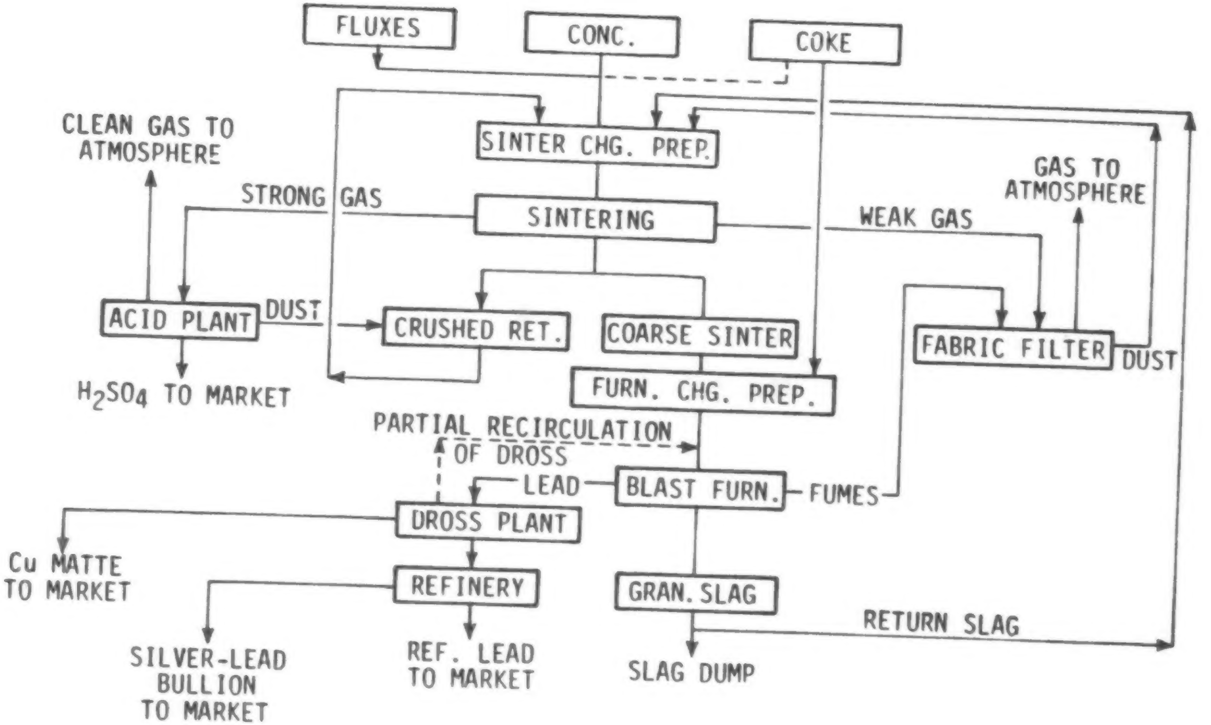
FLUXES
CONC.
COKE
CLEAN GAS TO ATMOSPHERE
SINTER CHG. PREP.
STRONG GAS
SINTERING
WEAK GAS
GAS TO ATMOSPHERE
ACID PLANT
DUST
CRUSHED RET.
COARSE SINTER
FABRIC FILTER
DUST
H_2SO_4 TO MARKET
FURN. CHG. PREP.
PARTIAL RECIRCULATION OF DROSS
LEAD
BLAST FURN.
FUMES
DROSS PLANT
Cu MATTE TO MARKET
REFINERY
GRAN. SLAG
RETURN SLAG
SILVER-LEAD BULLION TO MARKET
REF. LEAD TO MARKET
SLAG DUMP

Figure 4.8-2. Primary lead smelting--general flow sheet.[72]

are fairly low: retorting furnaces have a capacity of about 0.6 Mg (0.7 ton), while cupels can handle a maximum of approximately 11 Mg (12 tons) per charge.[71]

A total of five sintering machines and seven blast furnaces are used in the five domestic primary lead smelters. The sintering and blast furnace reduction processes are discussed in further detail in the following subsections.

4.8.1.1 Sintering Process--

The basic purpose of sintering is to convert most of the lead sulfide concentrate (PbS) into the oxide form while simultaneously producing a hard, porous, clinker material suitable for the rigid requirements of the blast furnace. About 85 percent of the sulfur is removed from the concentrate during sintering.[71] Figure 4.8-3 presents a typical flow sheet of a sintering plant.

The sintering machine is essentially a continuous, steel pallet-type conveyor belt that is motor-driven with appropriate gearing and sprockets. Each pallet consists of slotted grates. Either beneath or above the moving pallets are windboxes, which are connected to fans that provide a draft on the moving sinter charge. Depending on the direction in which the draft is placed upon the charge, the sintering machines are termed "updraft" or "downdraft." Because of their greater capacities, their lower maintenance and fan power requirements, and their ability to produce sinter of higher lead content, the updraft systems are more popular.[68]

Input to the sintering machine consists of lead concentrate, collected flue dusts, recycled sinter, and smelter residues. Sulfide-free fluxes are also added in most processses to maintain a specified sulfur content (5 to 7 percent by weight) in the charge. Silica and limestone are used as needed. Coke fines are also mixed with the charge.[71] Gas- or oil-fired burners are used to ignite the charge in updraft sintering machines. Water may be added for pelletizing the charge if the moisture content falls below required limits. Air is injected through the charge for oxidizing in the sintering machine.

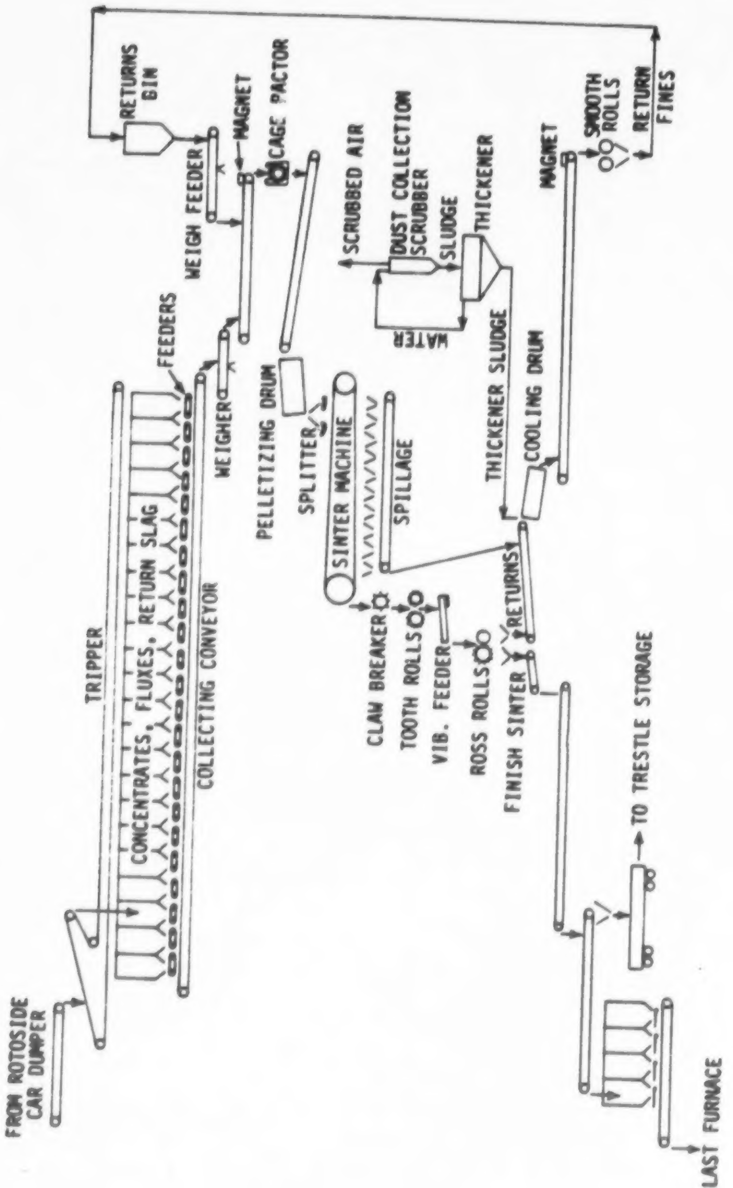
FROM ROTOSIDE CAR DUMPER
TRIPPER
CONCENTRATES, FLUXES, RETURN SLAG
COLLECTING CONVEYOR
FEEDERS
WEIGHER
WEIGH FEEDER
RETURNS BIN
MAGNET
CAGE PACTOR
PELLETIZING DRUM
SPLITTER
SINTER MACHINE
SPILLAGE
SCRUBBED AIR
DUST COLLECTION SCRUBBER
SLUDGE
THICKENER
WATER
THICKENER SLUDGE
COOLING DRUM
MAGNET
SMOOTH ROLLS
RETURN FINES
CLAW BREAKER
TOOTH ROLLS
VIB. FEEDER
ROSS ROLLS
FINISH SINTER
RETURNS
TO TRESTLE STORAGE
TO BLAST FURNACE

Figure 4.8-3. Flow sheet of a typical sinter plant.[73]

The sintering reaction is autogenous and creates temperatures of approximately 820°C (1500°F), the temperature basically controlled by the sulfur content of the charge. About 85 percent of the sulfur is removed from the concentrate during sintering. The exit gases may be removed in a single stream with an SO_2 concentration of about 2 percent, or split into two streams, one predominantly from the front and the other from the rear. The latter procedure produces both a weak (~0.5% SO_2) and a strong (~6.0% SO_2) SO_2 stream. The latter is amenable to sulfuric acid production.

An alternative solution to the elimination of the weak stream from the sintering machine is the use of weak gas recirculation, which can enable a single strong SO_2 gas stream (~6.0% SO_2) to be emitted.[68] This technique, however, is only used by foreign lead smelters.

Two of the existing domestic primary lead smelters use fabric filters for particulate control. Table 4.8-2 lists the controls used on lead sintering processes by U.S. smelters.

4.8.1.2 Blast Furnace Reduction Process--

The blast furnace is used in the primary lead industry to reduce sintered feed to a crude lead bullion. Figure 4.8-4 presents a flow sheet for the blast furnace reduction process.

Figure 4.8-5 allows a closer look at the blast furnace. The charge, which consists of sinter, metallurgical coke, and compounds such as limestone, silica, litharge, and other fluxing materials, is fed through a water-jacketed shaft at the top of the furnace. Coke comprises 8 to 15 weight percent of the furnace charge.[71] Combustion air is injected through tuyeres located near the bottom and evenly spaced on either side of the furnace. Oxygen is sometimes added to enrich the combustion air. Temperatures in the blast furnace range from 220°C (420°F) for the charge near the top of the furnace to 1210°C (2200°F) in the slag zone. Slag temperatures range from 980° to 1210°C (1800° to 2200°F), and bullion temperatures, from 890° to 960°C (1640° to 1750°F).

TABLE 4.8-2. ATMOSPHERIC CONTROL SYSTEMS ON DOMESTIC PRIMARY LEAD SINTERING MACHINES[71]

Plant and location	Control system
Amax, Boss, Missouri	Updraft sintering machine produces two gas streams: a strong gas stream that goes to the acid plant and a weak gas stream that is combined with blast furnace gas before it is discharged through the stack.
St. Joe, Herculaneum, Missouri	Updraft sintering machine produces two gas streams: a strong gas stream that goes to the acid plant and a weak gas stream that joins other gases and then passes through a fabric filter before exiting out the stack.
Asarco, Inc., E. Helena, Montana	Updraft sintering machine. Gases go to a water spray and an ESP; then dilution air is added and the gases are released out of the stack.
Asarco, Inc., Glover, Missouri	Updraft sintering machine. All gases go to a water spray and a fabric filter, and then out the stack.
Asarco, Inc., El Paso, Texas	Updraft sintering machine. A new control system is planned, which will make use of an acid plant for the strong stream.

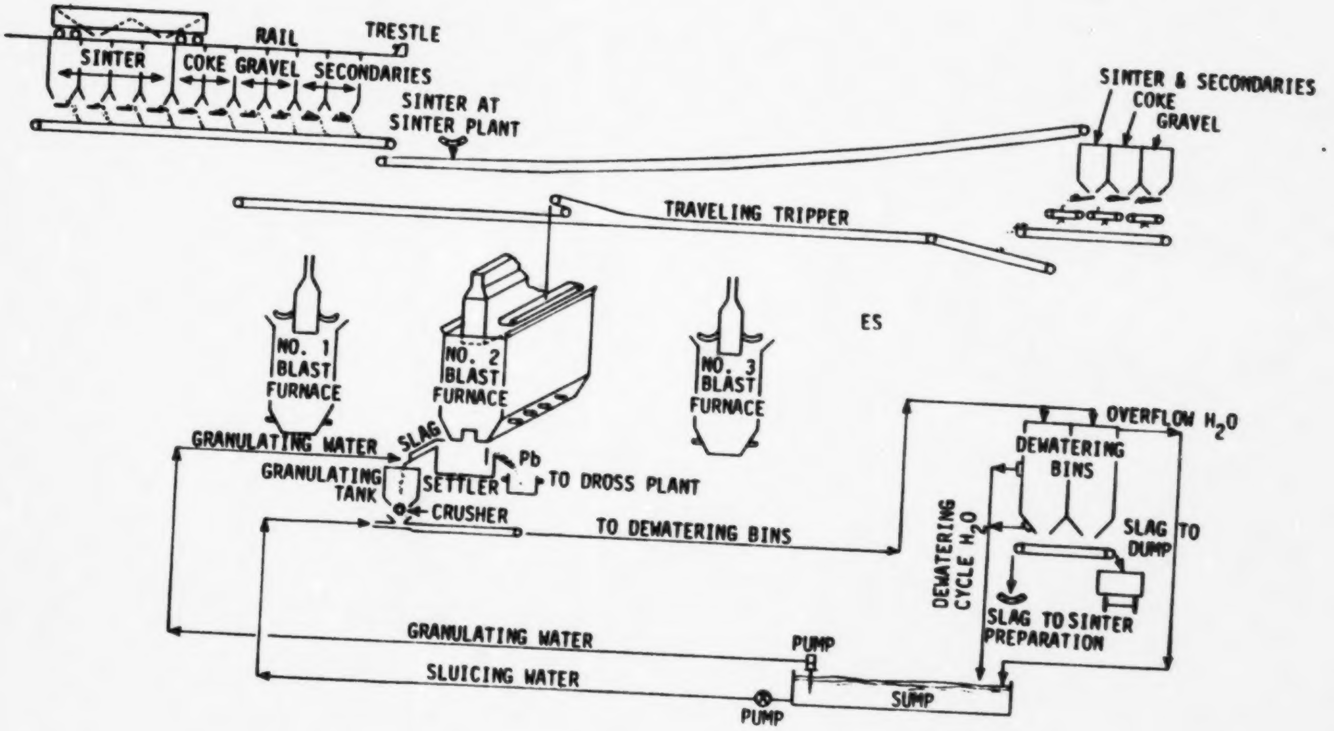
RAIL
TRESTLE
SINTER
COKE
GRAVEL
SECONDARIES
SINTER AT SINTER PLANT
SINTER & SECONDARIES
COKE
GRAVEL
TRAVELING TRIPPER
NO. 1 BLAST FURNACE
NO. 2 BLAST FURNACE
NO. 3 BLAST FURNACE
ES
GRANULATING WATER
SLAG
Pb
TO DROSS PLANT
GRANULATING TANK
SETTLER
CRUSHER
TO DEWATERING BINS
OVERFLOW H2O
DEWATERING BINS
DEWATERING CYCLE H2O
SLAG TO DUMP
SLAG TO SINTER PREPARATION
GRANULATING WATER
SLUICING WATER
PUMP
PUMP
SUMP

Figure 4.8-4. A flow sheet of a blast furnace reduction process.[73]

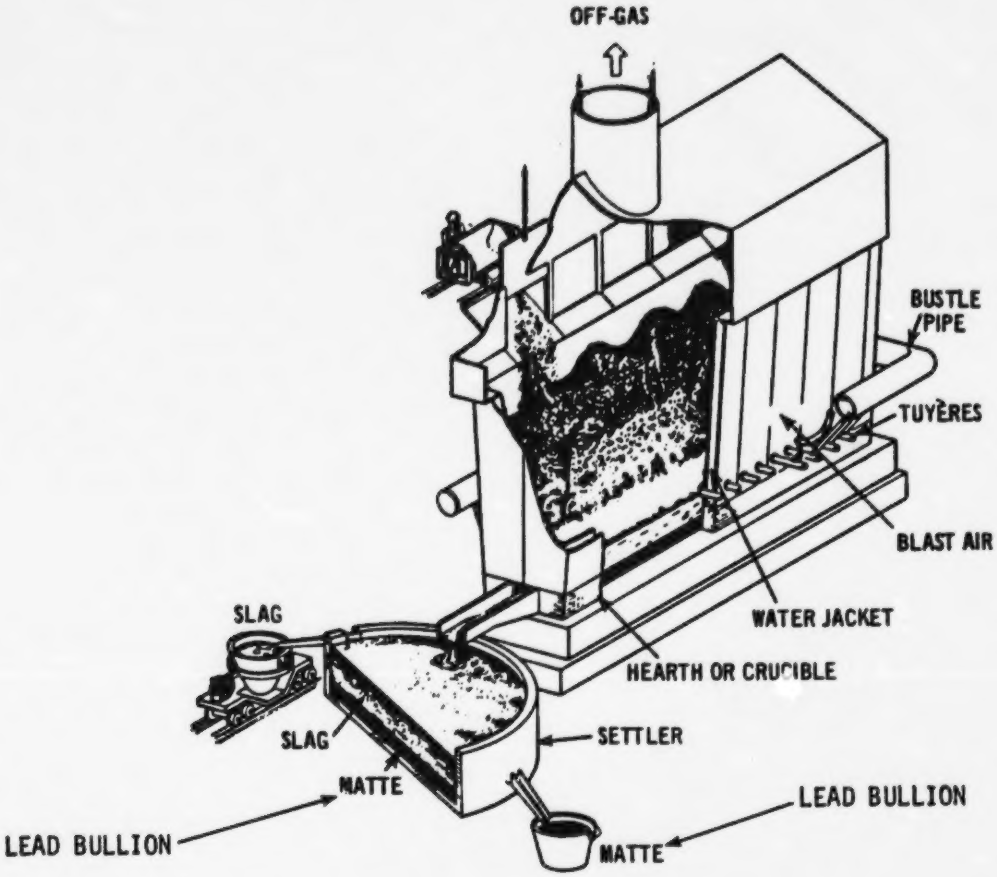
OFF-GAS
BUSTLE PIPE
TUYÈRES
BLAST AIR
WATER JACKET
HEARTH OR CRUCIBLE
SLAG
SLAG
SETTLER
MATTE
LEAD BULLION
LEAD BULLION
MATTE

Figure 4.8-5. Diagram of a lead blast furnace.[68]

The principal reactions that take place in the blast furnace are:[68]

$$PbO + CO + heat \rightarrow Pb + CO_2$$

$$C + O_2 \rightarrow CO_2 + heat$$

$$C + CO_2 + heat \rightarrow 2CO$$

Because the sintering process is not 100 percent efficient in the conversion of lead sulfide (PbS) to lead oxide (PbO), some lead sulfate ($PbSO_4$) and small amounts of lead sulfide remain in the product sinter. These compounds lead to additional lead-forming reactions and the simultaneous generation of SO_2.

$$2PbO + PbS \rightarrow 3Pb + SO_2$$

$$PbSO_4 + PbS \rightarrow 2Pb + 2SO_2$$

Sulfur dioxide concentrations range from a few hundred ppm to as much as 2500 ppm.[68] Sulfur dioxide emissions are not currently controlled.

Particulate emissions from lead blast furnaces are controlled by fabric filters at all the domestic smelters. Control efficiency ranges from 95 to 99.9 percent.[71] Table 4.8-3 describes the controls used for blast furnace gases.

4.8.2 Process Assessment for Hazardous Waste Destruction

A feasibility assessment was made of the use of the main processes in primary lead smelting for thermally destroying hazardous wastes.

The sintering process achieves a maximum temperature of only about 920°C (1500°F), which is not sufficient to destroy most of the hazardous wastes being considered in this study. Charging hazardous wastes in a safe manner also would be a problem with

TABLE 4.8-3. ATMOSPHERIC CONTROLS SYSTEMS ON DOMESTIC PRIMARY LEAD BLAST FURNACES[71]

Plant location	Control system
Amax, Boss, Missouri	Blast furnace gases join sinter weak gases, pass through fabric filters, and then exit out to stack.
St. Joe, Herculaneum, Missouri	Blast furnace gases join sinter weak gases and other gases, pass through the fabric filters, and then exit out the stack.
Asarco, Inc., E. Helena, Montana	Blast furnace gases join reverb and ventilation gases and then pass through three fabric filters in parallel, each with its own stack.
Asarco, Inc., Glover, Missouri	Blast furnace gases pass through a water spray, a fabric filter, and three stacks.
Asarco, Inc., El Paso, Texas	Blast furnace and dross furnace gases mix and then pass through a spray chamber and a fabric filter before they exit out of six stacks.

the sintering machine. Another disadvantage is the high potential for fugitive emissions. Also, the possible dilution of the strong SO_2 stream (amenable for H_2SO_4 production) by products of combustion of the hazardous wastes may result in a deterioration in the performance of the subsequent contact sulfuric acid plant. For the reasons just given, the sintering process has been eliminated from further consideration for hazardous waste disposal.

The lead refining process is essentially the final step in the formation of pure lead; hence, the introduction of extraneous materials, especially hazardous wastes, is not recommended for this process either.

Because of its high temperature [1210°C (2200°F)] and moderate residence times, the blast furnace reduction process, however, appears to be suitable for thermal disposal of hazardous wastes. The following subsections apply to the blast furnace process.

4.8.2.1 Technical Factors--

Compatibility of hazardous wastes with process fuel--Metallurgical coke is the primary fuel (as well as reducing agent) in the blast furnace reduction process. Because the main fuel is one of the reactants, the hazardous wastes cannot be substituted for any part of the fuel, but they can be introduced in addition to the coke. No compatibility problems are anticipated. The heat content of the wastes should be sufficient to sustain operating temperatures, and no additional process fuel (coke) is deemed necessary.

Graphical determination of suitable waste categories--

Process data--The typical blast furnace dimensions and operating data presented are based on blast furnace operations at the Herculaneum Lead Smelter of St. Joe Minerals Corporation, Herculaneum, Missouri.[73] The selected process conditions for determining the time-temperature relationship are as shown below:

Volume of blast furnace:	140 m^3 (4940 ft^3)
Gas volumetric flow rate:	276 Nm^3/min (10,500 scfm)
Maximum temperature:	1210°C (2200°F)
Exit gas temperature:	700°C (1300°F)

Approach--Based on computations of mean residence time (t) and fast-path residence time $\bar{t}$ for several temperatures below the maximum reaction zone temperature, process curves are plotted for the blast furnace reduction process and overlaid on the hazardous waste plots, as shown in Figure 4.8-6. Wastes in categories K015, K023, and K093 appear to be destructible.

Effects on product quality and product application--At the prevailing temperatures in the blast furnace, the hazardous constituents in the destructible wastes would undergo oxidation and/or thermal decomposition to other substances. The products of combustion would be emitted in the flue gas. No contamination of the lead bullion is expected.

Major areas of lead consumption include battery manufacturing, the production of gasoline additives, plumbing, and construction.[68,71] Any possible minor contamination is not expected to affect these applications either.

Impact on process hardware--No two blast furnaces are alike in dimensions or construction, which fact reflects a continual program to develop the most efficient design.[73] Most of the furnaces are of the Australian type, which have two rows of tuyeres. In the combustion and molten metal areas, the furnaces are generally constructed of fireclay brick about 1 foot thick. The hearth area is refractory lined. Furnace bullion is removed by refractory-lined transfer ladles. One of the destructible wastes, K015, contains halogens, and it is possible that the chlorides may affect the refractory lining.

Acceptable amounts of hazardous waste feed--Feed rates of input materials to the blast furnace vary from one plant to

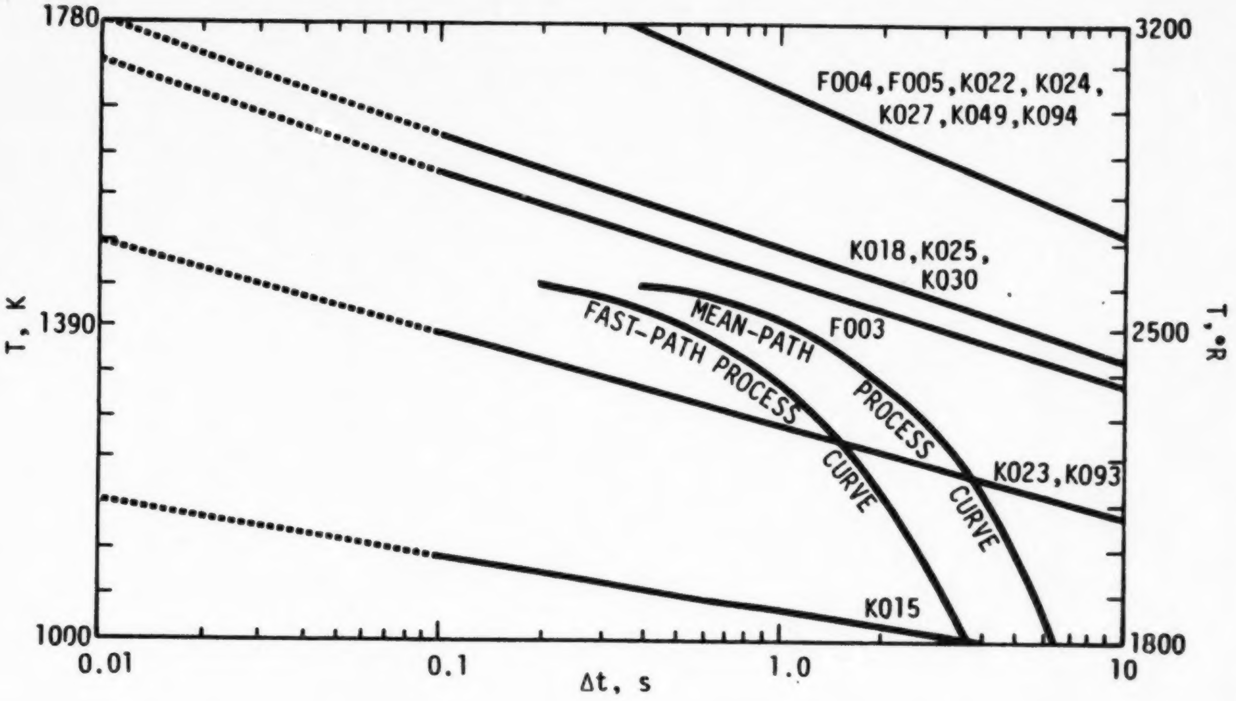

Figure 4.8-6. Hazardous waste destructibility predictions for blast furnaces in primary lead smelting.

another. Feed rates and smelting rates for a typical blast furnace are shown below:[73]

Sinter smelted	820 Mg/day (900 tons/day)
Size of charge, sinter	9.1 Mg (10 tons)
Coke in charge	9%
Air volume	276 Nm^3/min (10,500 scfm)

Assuming that the percentage of hazardous wastes in the charge is equivalent to that of coke in the charge, i.e., 9 percent by weight, then 734 Mg/day (81 tons/day) of hazardous waste can be destroyed.

Densities of the three destructible waste categories are as follows: K015, 1.64 kg/liter (13.7 lb/gal); K023, 1.37 kg/liter (11.4 lb/gal); and K093, 1.37 kg/liter (11.4 lb/gal). Assuming an average waste density of 1.44 kg/liter (12.0 lb/gal), the hazardous waste feed represents a consumption of 570 liters (150 gallons) per charge.

Provisions for waste introduction--The tuyeres available in the blast furnace for supply of combustion air could be used for introduction of the hazardous wastes. It might be preferable to introduce the atomized wastes through the lower set of tuyeres in Australian type blast furnaces. Modifications in the existing tuyere design would be necessary to atomize wastes before their introduction into the furnace. Domestic lead blast furnaces generally have 30 to 40 tuyeres at each level. These tuyeres have a diameter of 7.6 to 10 cm (3 to 4 inches).

Projected trends in process fuel--Because metallurgical coke serves the dual function of fuel and reductant in the blast furnace, no fuel substitution is possible and coke will remain the process fuel for lead blast furnaces. Additional sulfur introduced in the charge could minimize the amount of coke required.

4.8.2.2 Geographical Matching of Industry Location and Waste Generators--

Table 4.8-4 presents the geographic distribution of the destructible wastes and the SIC codes of the industries generating these wastes. The locations of the plants generating waste type K015 could not be determined. This table shows that none of the destructible waste types is generated in Missouri, where the majority of the domestic primary lead smelters are located. Significant quantities (38% of total) of waste K023 is generated in Illinois, however, which is a neighboring state to Missouri. Both K023 and K093 are also generated in Texas, where one of the primary lead smelters operated by Asarco is located.

TABLE 4.8-4. SIC CODES AND GEOGRAPHIC DISTRIBUTION OF INDUSTRIES GENERATING HAZARDOUS WASTES DESTRUCTIBLE IN PRIMARY LEAD SMELTING[19]

Hazardous waste categories	SIC codes of waste-generating industry	Geographic distribution of industries
K015	2865	Two plants (locations not known)
K023	2869	Richmond and El Sequendo, California; Kearney and Bridgeport, New Jersey; Baton Rouge, Louisiana; Bridgeville and Neville Island, Pennsylvania; Cicero and Millsdale, Illinois; Texas City, Texas
K093	2869	Texas, California, New Jersey

4.8.2.3 Environmental Factors--

Impact on air pollution control devices--Fabric filters are used to control particulates in blast furnace exhaust gases at all domestic primary lead smelters. Many of the fabrics commonly used as filter materials (e.g., Nomex, Teflon, and fiberglass) have excellent resistance to organic acids or solvents.[74] Hence, combustion products of hazardous wastes should have no harmful effect on the fabric filters.

Environmental impact--Not all sulfur in the sinter feed to the blast furnace is eliminated as SO_2. Almost half of the furnace sulfur is retained in the slag or matte.[68] Concentrations of SO_2 in the flue gas are therefore generally only a few hundred ppm. Concentrations of CO, however, are extremely high--around 25 to 50 percent.[71] Partial combustion of hazardous waste constituents could further increase CO levels. In lead smelting, afterburners are generally used to reduce CO concentrations to about 5 percent.[71] These should also control any additional CO due to waste combustion. Hydrocarbons would also be simultaneously controlled.

The fate of chlorides and fluorides resulting from the destruction of wastes in category K015 is an important consideration. Based on observed sulfur retention rates, it is expected that about 50 percent of the halogens would be retained as chlorides or fluorides in the slag and the remainder would be emitted with the flue gas. Emission measurements during test burns would help to determine accurately the fraction evolving with the flue gas.

Current disposal practices consist of conveying the slag hydraulically with a granulating water stream to a dump or tailings pond. Depending on the amount of halogens retained in the slag, the potential may exist for leaching of chlorides and fluorides as acids. This needs to be assessed in preliminary tests.

4.8.2.4 Institutional Factors--

Mine production and consumption of lead have declined since 1978, primarily because of curtailed use of lead antiknock compounds in gasoline.[71] Thus it is doubtful that any new smelters will be constructed in the United States in the near future. The industry currently employs about 2400 persons at smelters and refineries, and approximately 4700 people at mines.

Two of the primary lead smelters, St. Joe's Herculaneum smelter and Asarco's Glover smelter, are located 25 and 100 miles south of St. Louis, respectively, on the west bank of the Mississippi River. The setting of the Glover plant is rather typical of rural Missouri in the Ozarks.[75] The plant itself is surrounded by timber and cattle-grazing areas. Though easily accessible to rail and truck transportation, the plants are not close to population centers.

Many of the companies producing primary lead are vertically integrated and involved in two or more process segments. Some of these firms process other metals, such as zinc, copper, and gold, and the recovery of these metals often makes the mining and processing of lead economically feasible.[71] Because combustion of hazardous wastes is not likely to offer any cost benefits (such as fuel savings), it is doubtful that these facilities would be willing to accept wastes for destruction.

4.9 PRIMARY ZINC INDUSTRY

The major product of the primary zinc industry is metallic zinc, but zinc oxide, sulfuric acid, cadmium, and occasionally, zinc sulfate are also produced. Generally, ore is mined and concentrated at one location and then transferred to smelters for the production of zinc, zinc oxide, or both. Cadmium is normally recovered at smelters, from collected dusts and slags with sufficient cadmium content.[76]

Figure 4.9-1 shows the locations of the six existing domestic primary zinc smelters and Table 4.9-1 presents additional information regarding these smelters, including their capacities.

4.9.1 Process Descriptions

Zinc is usually found in nature as a sulfide ore called sphalerite, which also contains impurities of lead, cadmium, and

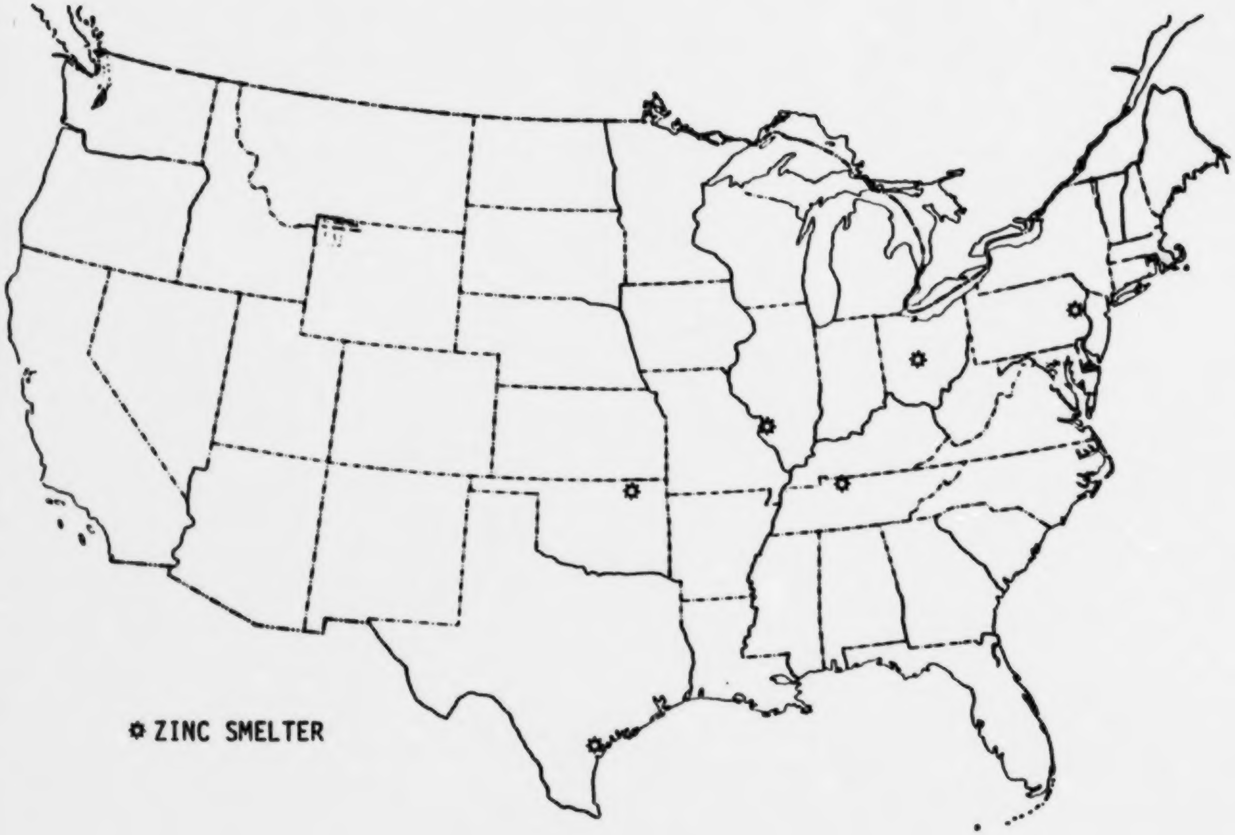
✿ ZINC SMELTER

Figure 4.9-1. Distribution of primary U.S. zinc smelters.[76]

TABLE 4.9-1. PRIMARY ZINC PROCESSING PLANTS IN THE UNITED STATES[76]

Company	Location	Process type	Design capacity, Mg/yr (tons/yr)	Date plant built
Amax, Inc.	East St. Louis, Illinois	Electrolytic	76,200 (84,000)	1929
Asarco, Inc.	Corpus Christi, Texas	Electrolytic	98,000 (108,000)	1942
	Columbus, Ohio	Pyrometallurgical	20,000 (22,000)	1967
Jersey Miniere Zinc	Clarksville, Tennessee	Electrolytic	89,900 (99,000)	1978
National Zinc Co.	Bartlesville, Oklahoma	Electrolytic	45,400 (50,000)	1977
New Jersey Zinc Co.	Palmerton, Pennsylvania	Pyrometallurgical	103,000 (113,000)	1899

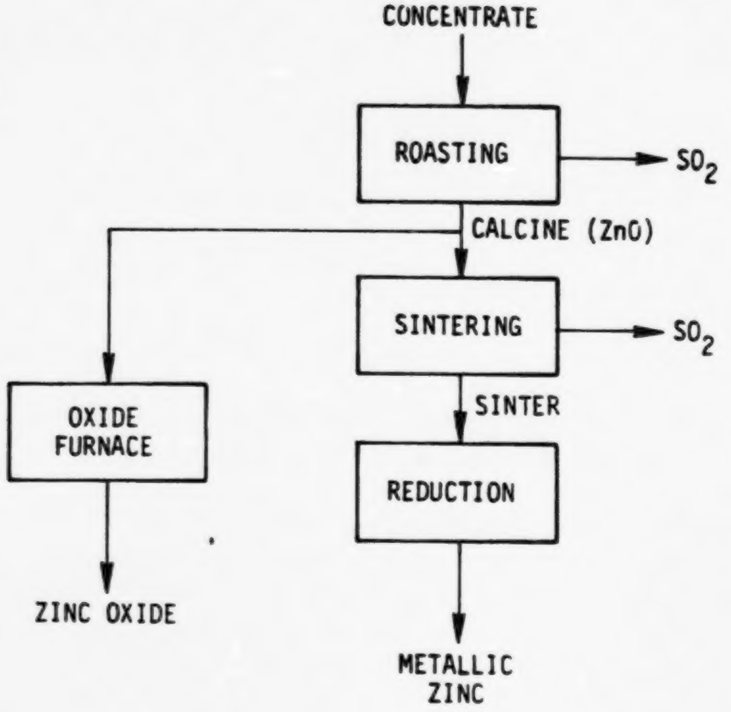
CONCENTRATE
ROASTING
SO_2
CALCINE (ZnO)
SINTERING
SO_2
SINTER
OXIDE FURNACE
REDUCTION
ZINC OXIDE
METALLIC ZINC

Figure 4.9-2. Flow diagram of primary pyrometallurgical zinc smelting process.[70]

minor amounts of other trace elements.[70] Generally, ore is mined and concentrated to about 62 percent zinc and 32 percent sulfur at one location, and then transferred to smelters for production of zinc and/or zinc oxide.

The smelting of zinc sulfide concentrates is carried out by either a pyrometallurgical or an electrolytic process, as illustrated in Figures 4.9-2 and 4.9-3. The initial roasting step, in which calcine is formed by removing most of the sulfur, is common to both processes. In the pyrometallurgical process, the calcine from the roasting step is sintered to form a dense, permeable feed for subsequent reduction to metallic zinc; whereas in the electrolytic process, the calcine is chemically leached and subjected to electrolytic extraction to produce 99.99+ percent pure, high-grade zinc.

The types of high-temperature furnaces employed in primary pyrometallurgical zinc manufacture are listed below:

1. Roasters: multiple-hearth, suspension (or flash), fluidized-bed
2. Sintering machines
3. Vertical/electrical retorts
4. Oxidizing furnaces: grate-type furnace, rotary (or Waelz) kiln, electrothermic furnace

Process details for these furnaces are presented in the following subsections.

4.9.1.1 Roasting Process--

Both zinc-smelting processes use one or a combination of several types of roasters to remove sulfur from the concentrate.

Multiple-hearth roasting--The multiple-hearth roaster, one of the oldest types of roasters, is currently used at only one smelter in the domestic industry. It is basically a cylindrical column 6.1 to 7.6 m (20 to 25 feet) in diameter with 7 to 16 hearths (see Figure 4.9-4). The reaction within the roaster is

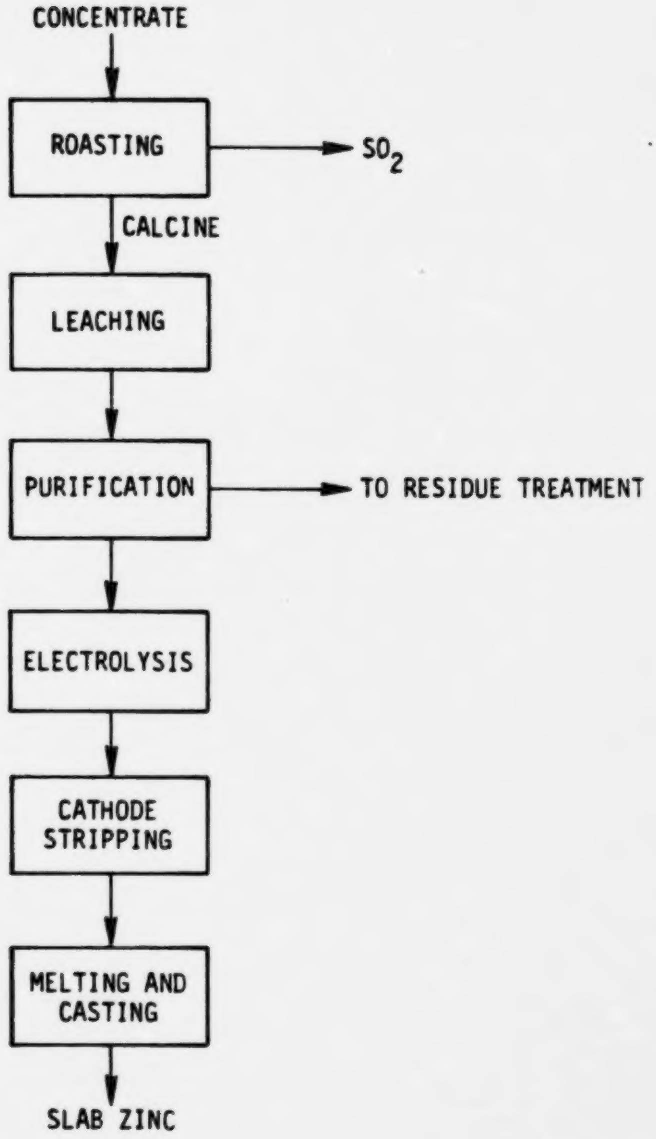
CONCENTRATE
ROASTING
SO_2
CALCINE
LEACHING
PURIFICATION
TO RESIDUE TREATMENT
ELECTROLYSIS
CATHODE STRIPPING
MELTING AND CASTING
SLAB ZINC

Figure 4.9-3. Flow diagram of primary electrolytic zinc smelting process.[70]

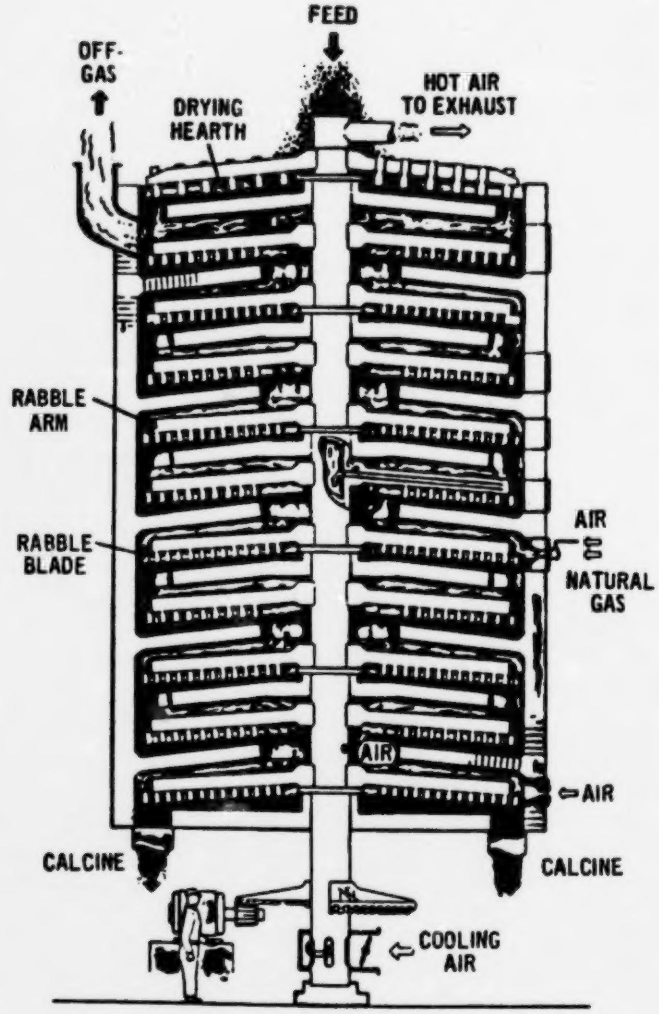
FEED
OFF-GAS
DRYING HEARTH
HOT AIR TO EXHAUST
RABBLE ARM
RABBLE BLADE
AIR
NATURAL GAS
AIR
AIR
CALCINE
CALCINE
COOLING AIR

Figure 4.9-4. Multiple-hearth roasting furnace.[70]

essentially autogenous. If enough sulfur is originally present as sulfide, the following reactions occur during roasting:[76]

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$ZnO + SO_3 \rightarrow ZnSO_4$$

In pyrometallurgical reduction, only the oxide state is desired; whereas in electrolytic reduction, small amounts of the sulfate state are acceptable.

Feed capacities for such roasters average 180 Mg (200 tons) per day.[76] Average operating temperature is about 690°C (1275°F), and the lower hearths are maintained around 980°C (1800°F). Operating time depends on the type of roaster, the composition of the concentrate, and the amount of sulfur removal required. Gas, coal, or oil must be added initially to bring the charge up to reaction temperature--about 1.2 GJ/Mg of ore (1×10^6 Btu per ton) is required for ignition.[76]

Off-gases from the roaster contain up to 7 percent sulfur, and are routed directly to "hot" ESP's operating at temperatures around 205°C (400°F), and then to an acid plant.[76]

Suspension roasting--Suspension, or flash, roasting is a process for rapid removal of sulfur and conversion of zinc to calcine by allowing the concentrates to fall through a heated oxidizing atmosphere or blowing them into a combustion chamber.[76] Figure 4.9-5 illustrates a flash roasting furnace.

The roasting process, which is similar to the burning of pulverized coal, achieves a higher heat transfer rate than multiple-hearth roasting does. The temperature in the combustion chamber is kept around 1010°C (1840°F). Chemical reactions occurring are the same as in multiple-hearth roasting.

The SO_2 concentration in the off-gases from flash roasting averages 10 to 13 percent, which is higher than that in the off-gases from multiple-hearth furnaces. The gases are cooled to

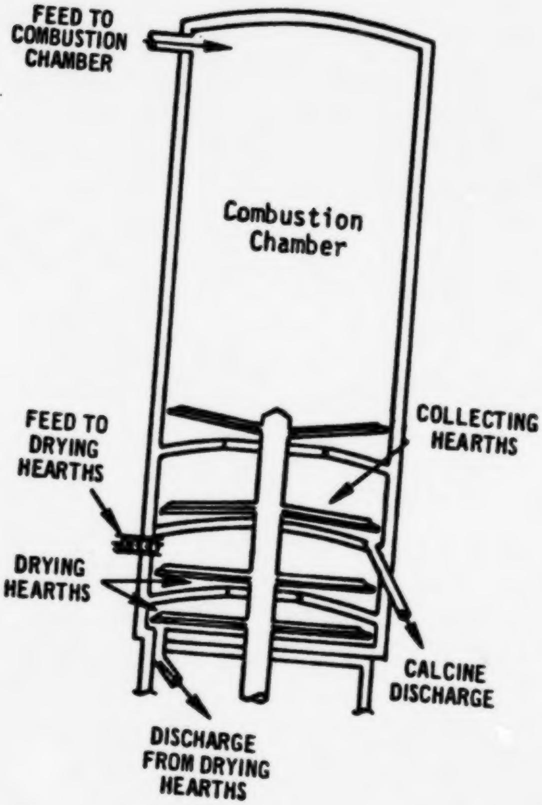
FEED TO COMBUSTION CHAMBER
Combustion Chamber
FEED TO DRYING HEARTHS
COLLECTING HEARTHS
DRYING HEARTHS
CALCINE DISCHARGE
DISCHARGE FROM DRYING HEARTHS

Figure 4.9-5. Suspension (flash) roasting furnace.[70]

about 400°C (750°F) in waste heat boilers, diluted with air, and humidified with water sprays before being sent to an ESP. The conditioned gases, which have an SO_2 concentration of 6 to 8 percent, are sent to an acid plant.

Fluidized-bed roasting--The fluid-bed roaster is the newest roasting system for zinc sulfide concentrates, and several domestic smelters are using it in different forms in both pyrometallurgical and electrolytic processes. The Amax and New Jersey Zinc smelters are examples.

Figure 4.9-6 illustrates a fluid-bed roaster. Roaster designs differ primarily in whether the roasters are charged with a wet slurry or a dry charge. Such roasters typically process 204 Mg (225 tons) per day of charge.[70] In the fluidized-bed process, no additional fuel is required after ignition has been achieved. Fluid-bed roasters operate at temperatures averaging 1000°C (1830°F); fluid column type roasters operate at temperatures approximately 38°C (100°F) higher. About 30 percent excess air is supplied.[77] Operating times vary, and they depend on the same factors as in other roasting processes. Natural gas, oil, or coal is used to bring the roaster feed to reaction temperatures, after which exothermic oxidation of sulfur maintains the bed temperature.

The off-gas, which contains approximately 12 percent SO_2 and exits the roaster at a temperature of about 950°C (1740°F), is cooled to 400°C (750°F) in waste heat boilers. Cyclones and ESP's are used for particulate control before the gas stream enters an acid plant.

4.9.1.2 Sintering Process--

As stated earlier, sintering of roasted charge is performed only in pyrometallurgical zinc smelting. Table 4.9-1 (presented earlier) lists only two pyrometallurgical primary zinc plants in the United States.

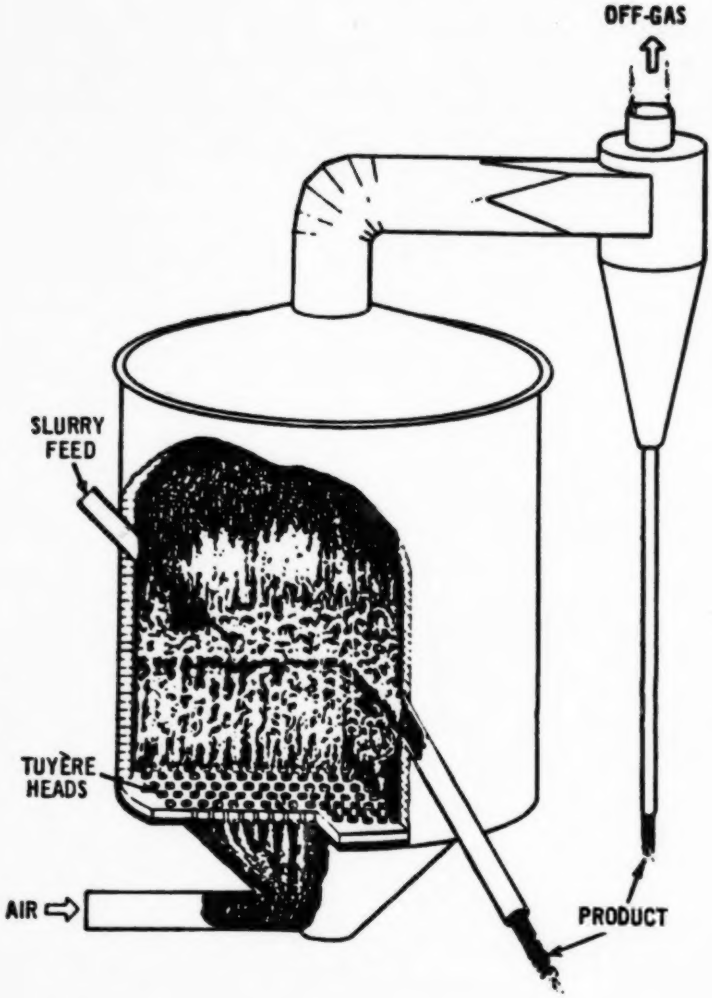
OFF-GAS
SLURRY FEED
TUYERE HEADS
AIR
PRODUCT

Figure 4.9-6. Fluid-bed roaster.[70]

The basic purpose of sintering in zinc smelting is the same as that for lead smelting, i.e., to produce a hard permeable mass suitable for feed to a reduction system. Sintering also volatilizes lead and cadmium impurities and discharges them into the off-gas stream, where they can be captured.

The sinter mix typically contains calcine, recycled sinter, coke or oil, sand, and other inert ingredients. Charging capacities typically range from 220 to 540 Mg (240 to 600 tons) per day. Typical operating conditions are 1040°C (1900°F) and atmospheric pressure.[76]

The sintering operation generates SO_2 and particulate matter. Because SO_2 concentrations are very low (0.1 to 2.4 percent), no SO_2 control is applied. Particulate control devices consist of various combinations of settling flues, cyclones, ESP's, and fabric filters.[76]

4.9.1.3 Retorting Process--

The retorting process is a continuous reduction/volatilization method for producing high-purity zinc from zinc oxide by reduction with carbon at elevated temperatures.[76] Depending on whether gas or electricity is used to supply the energy for reduction, the process is termed vertical retorting or electric retorting.

The primary reactions that occur in retorting consist of a reduction step and a CO regeneration step:

$$\text{ZnO} + \text{CO} \rightarrow \text{Zn (vapor)} + \text{CO}_2$$
$$\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$$

Both reactions are highly endothermic.

The feed to the retorts consists of sinter, coke, recycled zinc-bearing products, and additional binders, such as silica. No air is introduced in this reduction process. Maximum temperatures of about 1400°C (2550°F) are attained.

Emissions are minor compared with other processes in zinc smelting, such as roasting and sintering. Off-gases are cleaned by scrubbers, and because of their high CO content, serve as part of the fuel for heating the retorts.

4.9.1.4 Oxidizing Process--

This process occurs in zinc oxide production, where zinc vapor from sintering is immediately oxidized without being condensed. As with zinc metal production, zinc must first be produced in vapor form.

In the United States three types of furnaces are used for zinc oxide production: grate-type furnaces, rotary kilns, and electrothermic furnaces. Temperatures in the grate-type bed range from 980° to 1930°C (1800° to 3500°F); operating temperatures in rotary kilns are about 1320°C (2400°F). Temperatures in electrothermic furnaces vary from 900°C (1650°F) near the walls to about 1400°C (2550°F) in the main smelting zone.[76] All three furnace types emit some zinc oxide in the flue gas, and control techniques are similar to those used in other reduction operations.

4.9.2 Process Assessment for Hazardous Waste Destruction

Because roasting is the only step performed at all six domestic primary zinc smelters, it is this process that offers the greatest capacity for thermal disposal of hazardous wastes. Time-temperature requirements for all three types of roasters also appear compatible for hazardous waste destruction.

Sintering, retorting, and oxidizing processes only occur at the two domestic pyrometallurgical plants, and thus offer limited capacity for hazardous waste disposal. Possible difficulty with safely charging hazardous wastes and the inherent potential for high fugitive emissions are other disadvantages of the sintering process for hazardous waste destruction. The fact that no air is introduced in retorting excludes this process from consideration.

Rotary-kiln oxidizing furnaces would be suitable for waste destruction, but the limited number of such furnaces available does not make further consideration worthwhile.

In summary, only the roasting step in primary zinc smelting deserves further consideration with respect to hazardous waste disposal. Thus, the following subsections apply to the roasting process.

4.9.2.1 Technical Factors--

Compatibility of hazardous wastes with process fuel--Reactions occurring in all three roaster types are exothermic enough to be self-sustaining after ignition. Natural gas, oil, or coal is used to bring the charge up to reaction temperature. The lack of continuous addition of fuel in the process eliminates compatibility problems.

Graphical determination of suitable waste categories--

Process data--Multiple-hearth roasters are typically 6.1 to 7.6 m (20 to 25 ft) in diameter and 8.8 to 11 m (29 to 36 ft high).[70] The volume of off-gases leaving the multiple-hearth furnace ranges from 140 to 170 m^3/min (5000 to 6000 acfm) at 205°C (400°F).[76] The selected process conditions represent a roaster 6.1 m (20 ft) in diameter, 9.1 m (30 ft) high, with an off-gas volume of 170 m^3/min (6000 acfm). The chosen process parameters for multiple-hearth roasters can be represented as:

Working volume:	270 m^3 (9420 ft^3)
Gas volumetric flow rate:	97 Nm^3/min (3700 scfm)
Maximum reaction zone temperature:	980°C (1800°F)
Exit gas temperature:	205°C (400°F)

Suspension roasters are generally similar to multiple-hearth roasters in overall dimensions. Off-gas volumetric flow rates range from 280 to 420 m^3/min (10,000 to 15,000 acfm).[76] Based on a furnace 4.6 m (15 ft) in diameter, 6.7 m (22 ft) high, with an off-gas volumetric flow rate of 420 m^3/min (15,000 acfm), the following are the process conditions for suspension roasters:

Furnace volume: 111 m^3 (3900 ft^3)
Gas volumetric flow rate: 92 Nm^3/min (3500 scfm)
Maximum reaction zone temperature: 1010°C (1840°F)
Exit gas temperature: 927°C (1700°F) (assumed)

A fluidized-bed roaster having a diameter of 4.6 m (15 ft) and a height of 6.1 m (20 ft) is assumed based on dimensions reported in Reference 77. Typical off-gas volumetric flow rates range from 170 to 283 m^3/min (6000 to 10,000 acfm) at 950°C (1740°F).[76] The chosen conditions for determining the time-temperature relationship for fluidized-bed roasters are as follows:

Furnace volume: 99 m^3 (3500 ft^3)
Gas volumetric flow rate: 66 Nm^3/min (2500 scfm) based on 283 m^3/min at 950°C (10,000 acfm at 1740°F)
Maximum reaction zone temperature: 1000°C (1830°F)
Exit gas temperature: 950°C (1740°F)

Approach--For the assumed process conditions, computations of mean residence times (t) and fast-path residence times ($\bar{t}$) were made for each of the three roaster types for several temperatures below the maximum reaction zone temperature. These computations enabled the plotting of process curves for the three roasting processes, as shown in Figures 4.9-7, 4.9-8, and 4.9-9. Wastes in category K015 appear to be destructible in all three roasters. Wastes in categories K023 and K093 also appear destructible in suspension and fluidized-bed roasters.

Effects on product quality and product application--No harmful impact on product (zinc/zinc oxide) quality is expected

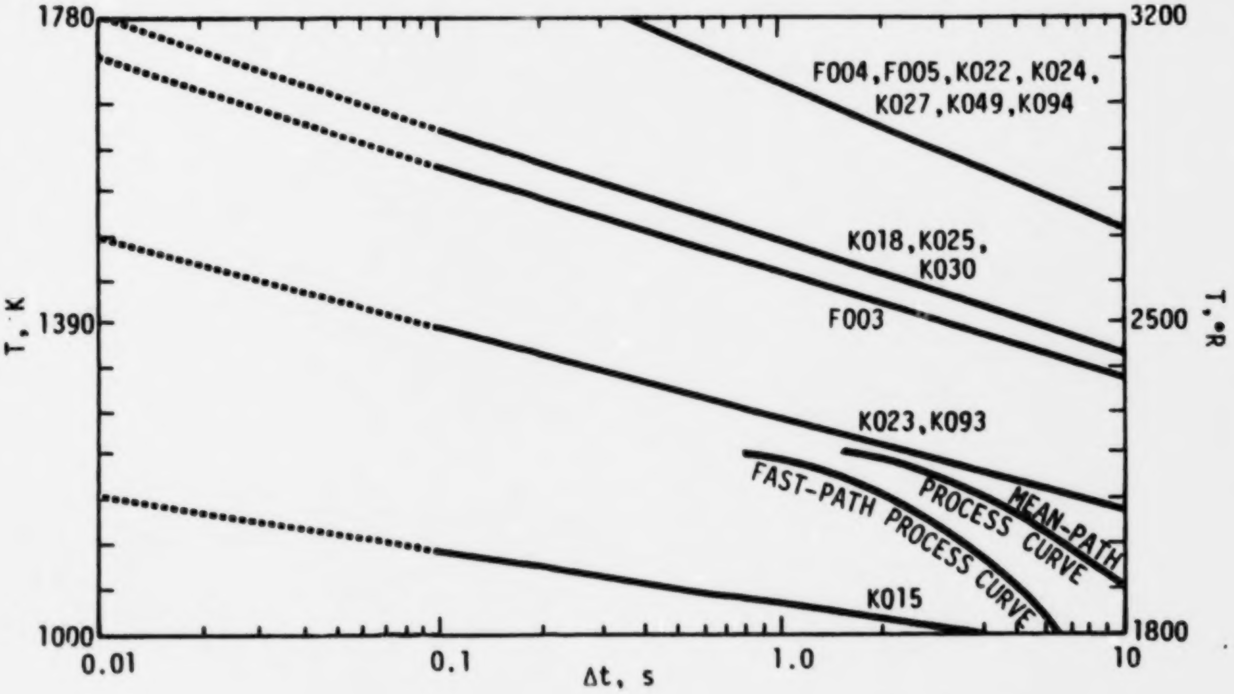

Figure 4.9-7. Hazardous waste destructibility predictions for multiple-hearth roasters in zinc smelting.

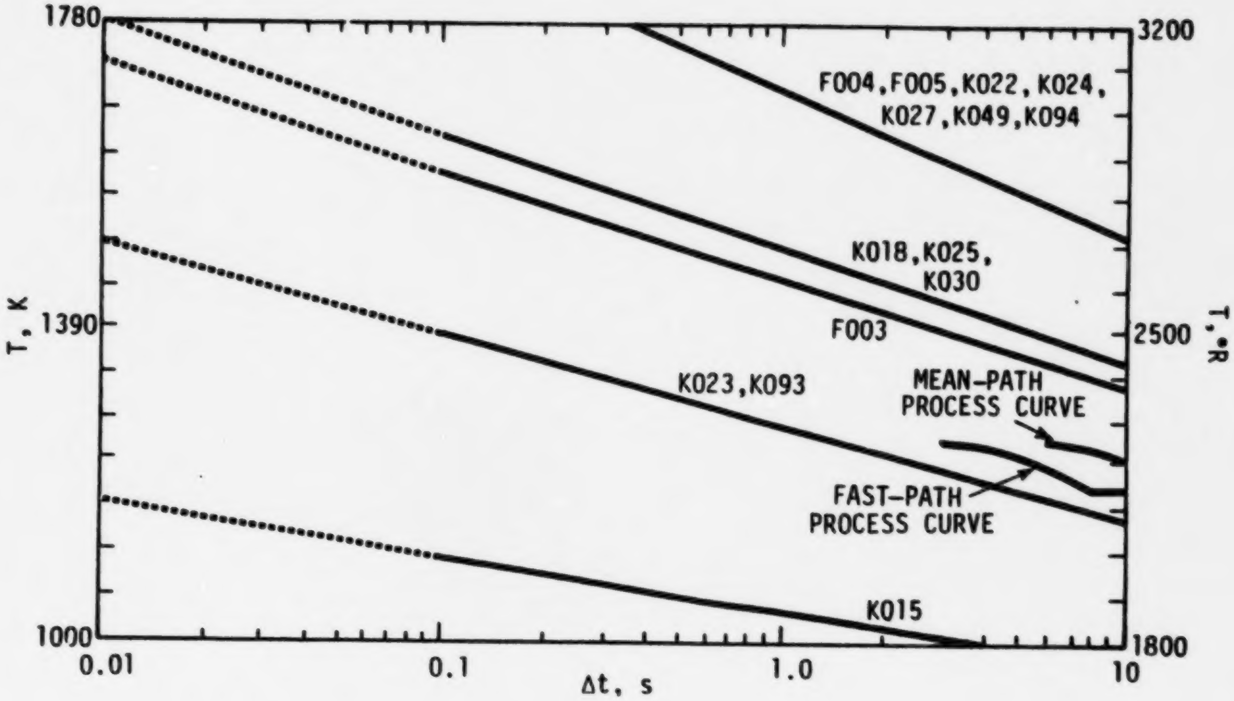

Figure 4.9-8. Hazardous waste destructibility predictions for suspension roasters in zinc smelting.

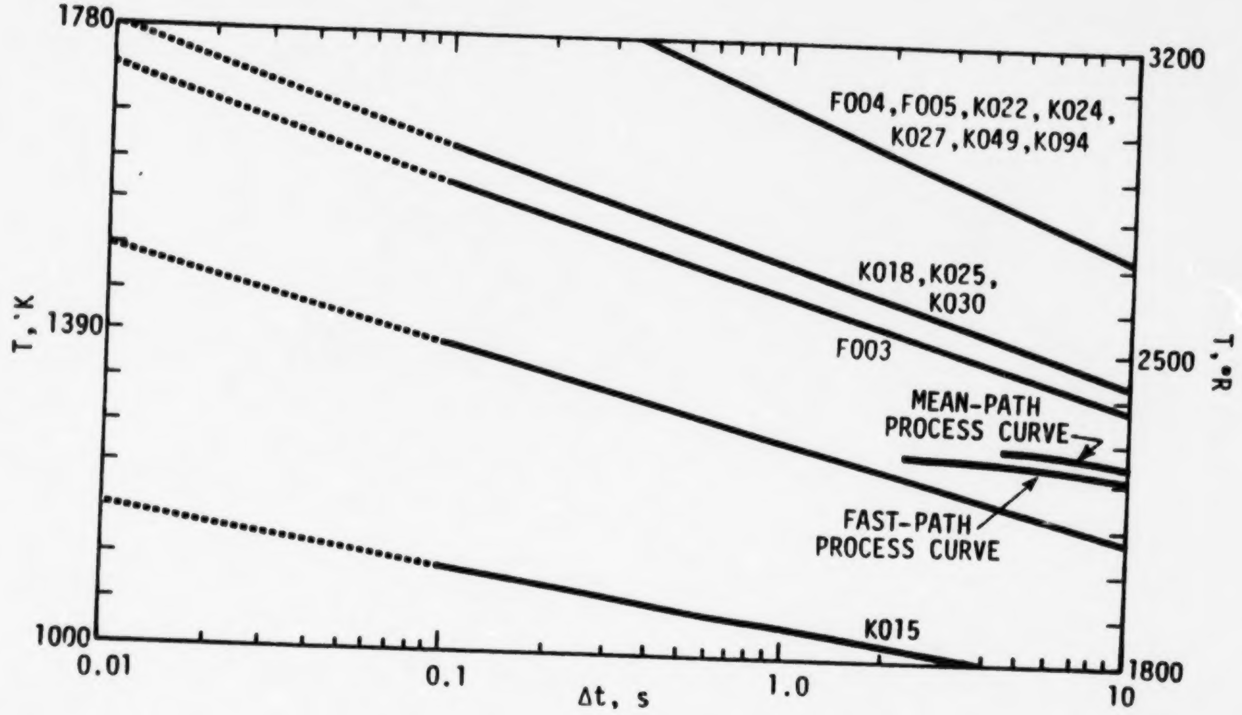

Figure 4.9-9. Hazardous waste destructibility predictions for fluidized-bed roasters in zinc smelting.

from the combustion of hazardous wastes in the roasters. It should be noted, however, that if the hazardous waste contains sufficient sulfur, additional formation of zinc sulfate ($ZnSO_4$) might occur in the roasters, which is not very desirable, especially in pyrometallurgical zinc smelting. Moreover, bed temperatures would have to be monitored closely to assure calcine quality.

Any possible minor contamination of the product, however, should not be cause for concern in the predominant zinc applications in galvanizing and alloying.

Impact on process hardware--The roasters are generally brick-lined, cylindrical steel columns covered with insulation. In suspension roasters, problems have resulted from the steel shells becoming too hot because of over-insulation.[78] Because such problems could be compounded during the firing of hazardous wastes, it is necessary that the right insulation thickness be maintained to prevent sulfation and corrosion that occur at the higher temperatures.

When hazardous wastes are fired in multiple-hearth roasters, it is recommended that the high-temperature hearths be continuously checked for plugups. In normal practice, hard accretions that form on the hearths necessitate a routine maintenance maneuver called "plowing," the frequency of which varies from 2 to 3 days for high-temperature hearths to 2 to 3 months for those operating at low temperatures.[79] The frequency of cleaning may have to be increased when firing hazardous wastes.

The destruction of hazardous wastes in the furnaces may necessitate improved maintenance procedures for screw conveyors and waste heat boilers (in the case of suspension and fluidized-bed roasters only).

Acceptable amounts of hazardous waste feed--Because fuel is generally not added to the roasters on a continuous basis, estimates of quantities of hazardous wastes destructible in roasters can be based on concentrate feed rates.

Typical concentrate feed rates to all three types of roasters average about 181 Mg (200 tons) per day. Assuming that the hazardous wastes represent 10 percent by weight of the charge, hazardous waste feed rate would be about 18.1 Mg/day (20 tons/day).

Densities of the three waste categories that are believed to be destructible in the roasters are as follows:

K015: 1.64 kg/liter (13.7 lb/gal)
K023: 1.37 kg/liter (11.4 lb/gal)
K093: 1.37 kg/liter (11.4 lb/gal)

Assuming an average density of 1.44 kg/liter (12 lb/gal), the hazardous waste feed rate represents a consumption of 12.6 kl (3330 gal) per day.

Provisions for waste introduction--In the case of the multiple-hearth roasters, the hazardous wastes should be atomized and introduced near the lower hearths of the furnace because this is where roaster temperatures are highest. "Snowballing" of concentrates should be avoided, especially when charging hazardous wastes, by maintaining temperatures in the desired range.

The suspension roaster has a large combustion space at the top and two to four hearths similar to those of a multiple-hearth furnace in the lower portion. The zinc concentrates are introduced near the top of the combustion chamber. It would be preferable to introduce the atomized hazardous wastes near this point to allow adequate residence time in the combustion space. The off-gases generally exit from a point near the top of the hearths, close to the bottom of the free combustion space.

Fluidized-bed roasters are equipped with tuyeres at the bottom to supply fluidizing air, and the hazardous wastes could be introduced through these tuyeres. Modifications in tuyere design, however, would be needed for atomizing the liquid wastes.

Projected trends in process fuel--The energy requirement for the roasting process is about 1.2 GJ/Mg (1 x 10^6 Btu/ton) of ore, which is consumed during initial ignition. Exothermic oxidation of sulfur in the ore maintains operating temperatures beyond this point. Gas, coal, and oil have been used to bring the charge to reaction temperatures; natural gas is the primary fuel.[76]

4.9.2.2 Geographical Matching of Industry Location and Waste Generators--

Table 4.9-2 presents the SIC codes and geographic distribution of the industries generating the waste categories that are destructible in the zinc ore roasting process. The geographic distribution information allows a matching of the waste generator and primary zinc smelting industry location. Waste categories K023 and K093 are both generated in Texas, where an electrolytic smelter operated by Asarco, Inc., is located. Category K023 wastes are also generated in Illinois and Pennsylvania, and each of these States has a primary zinc smelter in operation (see Table 4.9-1). Thus, the matching between industry location and generators of destructible hazardous waste categories seems to be good. Destructible wastes are also generated in significant quantities in California and New Jersey; however, no zinc smelters are located in either of these states.

TABLE 4.9-2. SIC CODES AND GEOGRAPHIC DISTRIBUTION OF INDUSTRIES GENERATING HAZARDOUS WASTES DESTRUCTIBLE IN THE ZINC ORE ROASTING PROCESS[19]

Hazardous waste category	SIC code for waste-generating industry	Geographic distribution of industries
K015	2865	Two plants (locations unknown)
K023	2869	Richmond and El Sequendo, California; Kearney and Bridgeport, New Jersey; Baton Rouge, Louisiana; Bridgeville and Neville Island, Pennsylvania; Cicero and Millsdale, Illinois; Texas City, Texas
K093	2896	Texas, California, New Jersey

4.9.2.3 Environmental Factors--

Impact on air pollution control devices--Electrostatic precipitators are used to control particulate emissions from all three types of roasters. Cyclones and waste heat boilers precede the ESP's in the case of suspension and fluidized-bed roasters. About 20 percent of the suspended dust settles out in the waste heat boilers, and more than 99.5 percent of the remaining particulates are removed in the final particulate control equipment. Any additional particulate emissions due to waste combustion should be adequately controlled by the ESP's.

Concentrations of SO_2 in roaster off-gases are sufficiently high for production of sulfuric acid; however, contact acid plants operate efficiently only when the gas stream being processed meets certain desirable characteristics. The gas stream should have a consistent flow rate, be almost completely dried, and contain no fumes or gases that may poison the catalyst in the acid plant catalytic converter.[76] Sulfur dioxide concentrations of at least 7 percent are desirable. Combustion of hazardous wastes in the roasters could have an undesirable effect on the properties of the off-gases for subsequent acid production. Final traces of objectionable materials that could result from hazardous waste combustion can be removed by special scrubbers, which are usually available at the acid plant. Off-gas analysis measurements obtained during test burns should help to identify other problem areas.

Environmental impact--Roasting processes do not generate any solid or process-water waste; however, for the suspension and fluid-bed roasters, there is a boiler blowdown from the waste heat boiler. In all the roasting processes, solids are recycled to recover byproduct metals.[76] Thus, combustion of hazardous wastes in the roasters is not expected to have any harmful impact on the environment.

4.9.2.4 Institutional Factors--

Although the primary domestic zinc smelting capacity has been declining since 1968, U.S. primary zinc demand is expected to increase at an annual rate of 2 percent through 1985. Zinc smelters employed about 4100 people in 1978, including workers involved in byproduct processes.[76] The smelters are generally located away from population centers.

The main uses of zinc are for galvanizing, alloying, and grinding into zinc dust. These applications are such that the customer would not be concerned about the impact of the waste on the zinc product. Also, zinc smelting facilities are not expected to have any major objections to accepting hazardous wastes.

4.10 SEWAGE SLUDGE INCINERATORS

4.10.1 Process Descriptions

The two major types of sewage sludge incinerators used in the United States are the multiple-hearth and the fluid-bed.[80] A third type is the flash-drying arrangement used in conjunction with a fossil-fuel or refuse-fired furnace. This type is not discussed in this report.

4.10.1.1 Multiple-Hearth Incinerator--

The multiple-hearth incinerator is currently the most widely used sewage sludge incinerator in the United States. As of 1977, approximately 340 units had been installed for wastewater sludge combustion. This incinerator is durable and relatively simple to operate, and it can handle wide fluctuations in feed quality and loading rates.

The multiple-hearth incinerator consists of vertically stacked hearths raked by rabble arms rotated from a common shaft.[81] Dewatered sludge is fed to the top hearth, and is plowed to drop holes by the rotating rabble arms. It falls to the next hearth and then the next until ash is discharged at the bottom.[82]

Because the sludge is constantly turned and broken into smaller particles as it moves across the hearths, a large surface of the sludge is exposed to the hot furnace gases. This process includes rapid and complete drying as well as combustion. As shown in Figure 4.10-1, the system has three operating zones: 1) the top hearths, where sludge feed is dried to about 48 percent moisture; 2) the incineration/deodorization zone, where the temperature is 760° to 980°C (1400° to 1800°F); and 3) the cooling zone, where the hot ash gives up heat to incoming combustion air. Exhaust gases exit at 430° to 540°C (800° to 1000°F).

Figure 4.10-2 shows an interior cut-away view of the multiple hearth incinerator. The central shaft of the furnace is a hollow iron column cast in sections; shaft speeds are adjustable from about 1/2 to 1-1/2 revolutions per minute. The hollow rabble arms are connected to machined arm sockets in the shaft. The shaft and rabble arms are air-cooled and normally insulated. A cold air tube runs up the center of the shaft. Air lances extend from the cold air tube out to the ends of each rabble arm. Ambient air of regulated pressure and volume is forced through the cold air tube and lances by means of a blower. The cold air exits from the tips of the lances and flows backward through the space between the lances and the rabble arm walls to the annular space in the central shaft (known as the hot air compartment). The flow of air cools the arms. The air is conducted through the hot air compartments to cool the shaft, and then is either discharged to the atmosphere via the exhaust gas stack or returned to the bottom hearth of the incinerator as preheated air for combustion.[80] Excess air requirements are generally 75 to 100 percent.

4.10.1.2 Fluid-Bed Incinerator--

There are approximately 60 operating fluid-bed sludge incinerators in the United States.[80] The fluid-bed incinerators are versatile devices that can be used to dispose of solid, liquid,

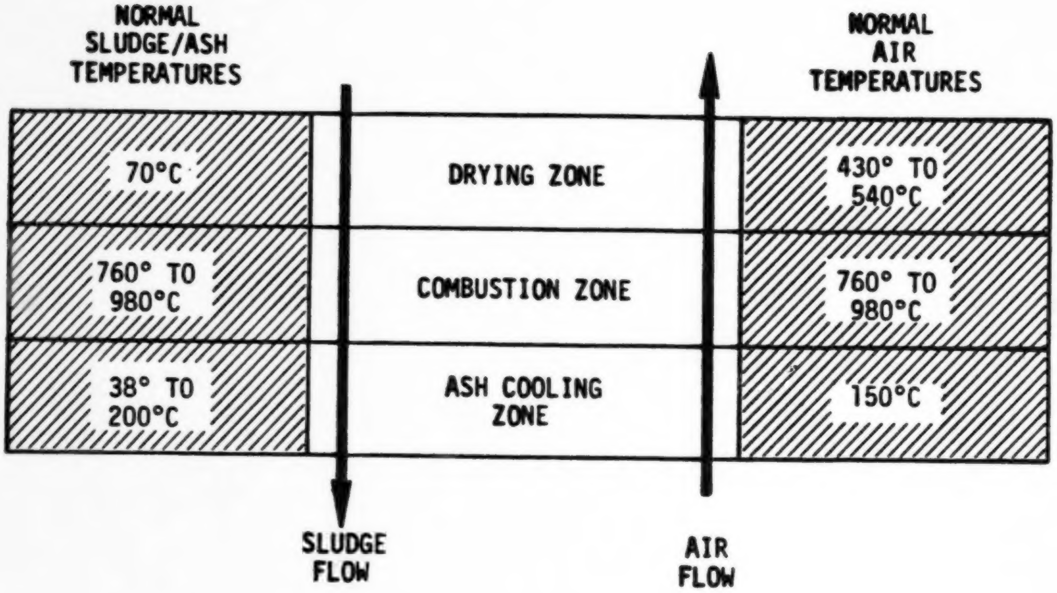
NORMAL SLUDGE/ASH TEMPERATURES
NORMAL AIR TEMPERATURES
70°C
DRYING ZONE
430° TO 540°C
760° TO 980°C
COMBUSTION ZONE
760° TO 980°C
38° TO 200°C
ASH COOLING ZONE
150°C
SLUDGE FLOW
AIR FLOW

Figure 4.10-1. Process zones in multiple-hearth incinerator.

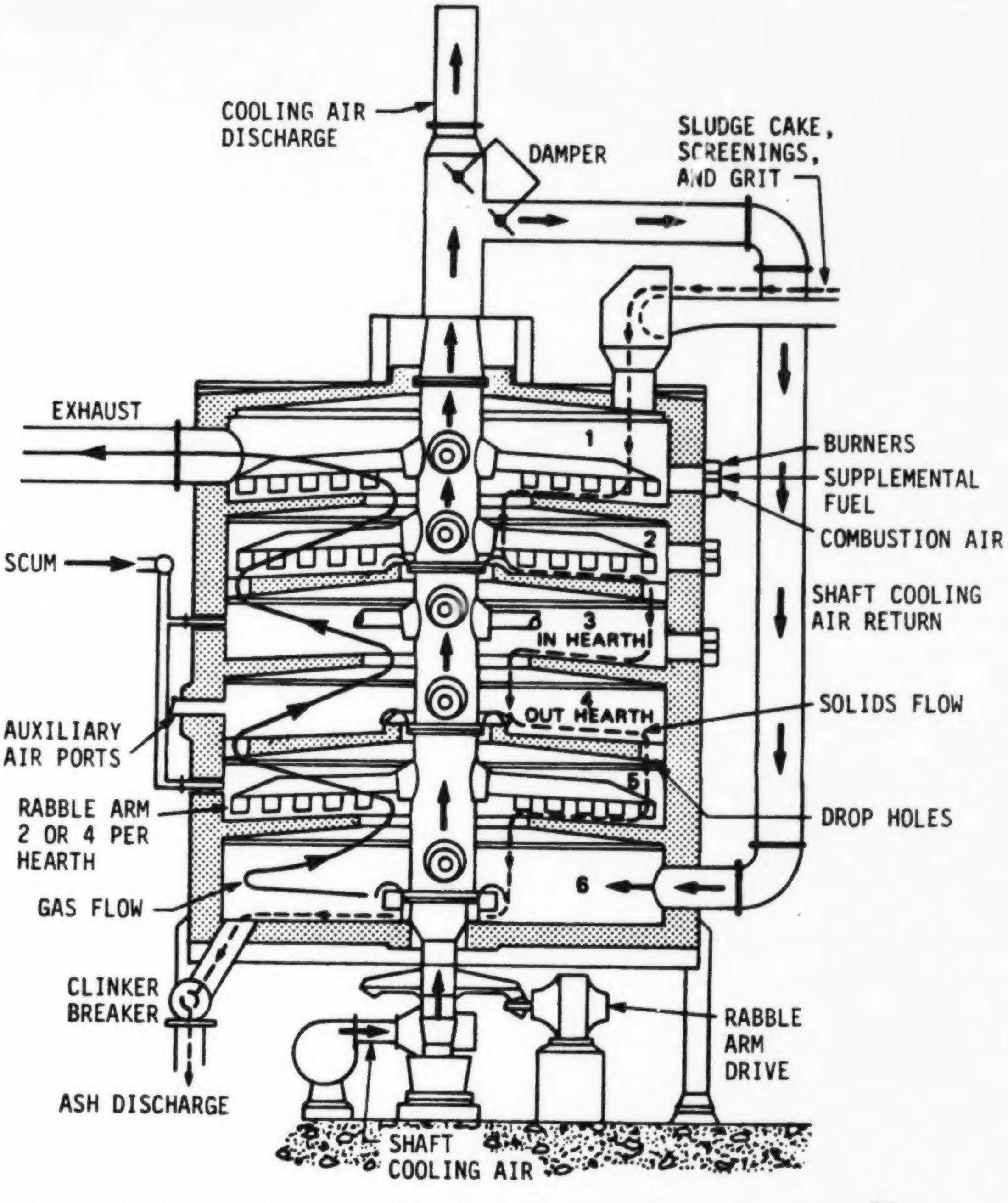
COOLING AIR DISCHARGE
DAMPER
SLUDGE CAKE, SCREENINGS, AND GRIT
EXHAUST
BURNERS
SUPPLEMENTAL FUEL
COMBUSTION AIR
SCUM
SHAFT COOLING AIR RETURN
1
2
3
IN HEARTH
4
OUT HEARTH
5
6
SOLIDS FLOW
AUXILIARY AIR PORTS
DROP HOLES
RABBLE ARM 2 OR 4 PER HEARTH
GAS FLOW
CLINKER BREAKER
RABBLE ARM DRIVE
ASH DISCHARGE
SHAFT COOLING AIR

Figure 4.10-2. Cross section of a multiple-hearth incinerator.[80]

or gaseous combustible wastes. They are vertically oriented and cylindrically shaped and have a refractory-lined steel shell that contains a sand bed and fluidizing air diffusers. Air that is driven by a blower enters at the bottom of the incinerator and rises vertically through a distributor plate into a vessel containing a bed of inert granular particles or sand. The upward flow of air through the sand bed results in a dense turbulent mass that behaves much as a liquid would. Waste material to be incinerated is injected into the bed, where combustion occurs within the fluidizing media. Air passage through the bed produces strong agitation of the bed particles, which promotes rapid and relatively uniform mixing of the ignited waste material within the fluidized bed.[82] Figure 4.10-3 shows a cross section of a fluid bed incinerator.[80]

Bed temperatures are quite uniform and typically in the range of 760° to 870°C (1400° to 1600°F). The bed expands to approximately 100 percent of its rest volume. In essence, the reactor is a single chamber unit in which both drying and combustion occur in either dense or dilute phases in the sand bed. All of the combustion gases pass through the combustion zone, where the residence time is several seconds. Ash is carried out the top of the furnace and is removed by air pollution control devices, usually a venturi scrubber. Feed to the incinerator is introduced either above the bed or directly into it.[80] Excess air requirements for the fluid-bed incinerator vary from 20 to 40 percent.

4.10.2 Process Assessment for Hazardous Waste Destruction

Both the multiple-hearth and fluid-bed incinerators appear to be feasible for thermal destruction of some hazardous wastes. Both have the capability of attaining moderately high combustion temperatures and have relatively long residence times. Also, these sewage sludge incinerators are durable and designed to handle wide fluctuations in feed quality and loading rates.

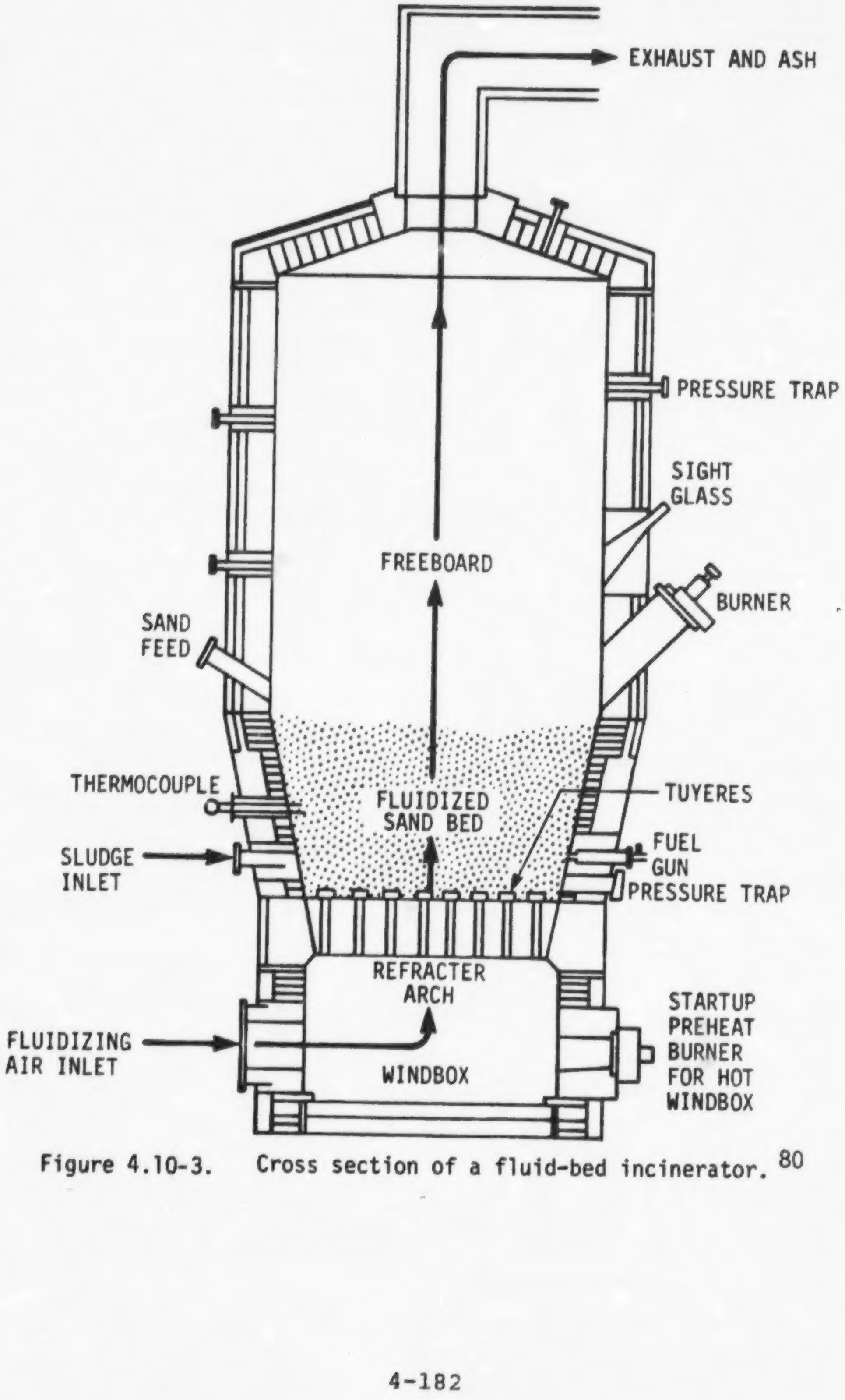
EXHAUST AND ASH
PRESSURE TRAP
SIGHT GLASS
FREEBOARD
BURNER
SAND FEED
THERMOCOUPLE
FLUIDIZED SAND BED
TUYERES
SLUDGE INLET
FUEL GUN
PRESSURE TRAP
REFRACTER ARCH
STARTUP PREHEAT BURNER FOR HOT WINDBOX
FLUIDIZING AIR INLET
WINDBOX

Figure 4.10-3. Cross section of a fluid-bed incinerator.[80]

4.10.2.1 Technical Factors--

Compatibility of hazardous wastes with process fuel--The compatibility of co-incinerating hazardous waste with sewage sludge is dependent on several factors: physical state and chemical composition of the hazardous waste, method of injection currently used at the incinerator, and the type of air pollution control device used. Virtually any material that can be burned can be combined with sludge in a co-combustion process.

For successful incineration, the sludge feed composition and the volatile solids content are important. Both multiple-hearth and fluid-bed incinerators provide adequate mixing of the feed with combustion gases and a residence time that insures complete combustion of sludge. For incineration of hazardous wastes, however, it may be necessary to keep temperatures higher than normal to meet the recommended destruction efficiencies. The physical state of the hazardous waste will determine which method of waste injection is most appropriate. With proper mixing, waste liquids and sludges generally can be added directly to the sewage sludge and then introduced to the incinerator. Hazardous waste can be combined with the sewage sludge in a mixing tank if proper handling practices are used. This will eliminate the need for a second feed system to handle the hazardous waste.

Proper mixing of the hazardous waste and sewage sludge is important. The feed rate of the hazardous waste should be based on 10 percent of the total heat value imput. Sludge heat value is fairly high [12 to 23 kJ/kg (5000 to 10,000 Btu/lb) dry solids]; however, the water content of most sludges requires the addition of auxiliary fuel to maintain combustion in the furnace.

Graphical determination of suitable waste categories--The criteria for determining the potential destructibility of various hazardous wastes are the time-temperature relationships. Residence time and temperatures of typical sewage sludge incinerators are as follows:

	Fluid-bed	Multiple-hearth
Maximum temperature	870°C (1600°F)	980°C (1800°F)
Exit temperature	760°C (1400°F)	430°-540°F (800°-1000°F)
Residence time	5-6 s	5 s

Figures 4.10-4 and 4.10-5 are graphic representations of the relationship of Δt and $\Delta \bar{t}$ (mean and fast-path) versus T for typical multiple-hearth and fluid-bed incinerators. The temperature-time requirements for 99.99 percent destruction of the hazardous wastes are also plotted on this graph. Because of this graph, predictions can be made regarding the probability or feasibility of meeting the 99.99 percent destruction efficiency for each hazardous waste in a sewage sludge incinerator. Results are summarized in Tables 4.10-1 and 4.10-2. It appears that none of the hazardous wastes considered in this report can be thermally destroyed in a multiple-hearth incinerator under normal operating conditions. The destruction of hazardous waste category K015 is, however, marginally feasible in a fluid-bed incinerator. Destruction of other hazardous wastes may be feasible in either furnace type if operating temperatures were increased.

Effects on product quality and product application--The incineration of sewage sludge is a waste treatment process with no end product; therefore, the question of waste impact on product quality does not arise.

Impact on process hardware--The reactors of both multiple-hearth and fluid-bed incinerators are generally refractory-lined steel, and the central shaft of the multiple-hearth incinerator is cast iron.[82] These construction materials should not be adversely affected by the inclusion of hazardous waste in the

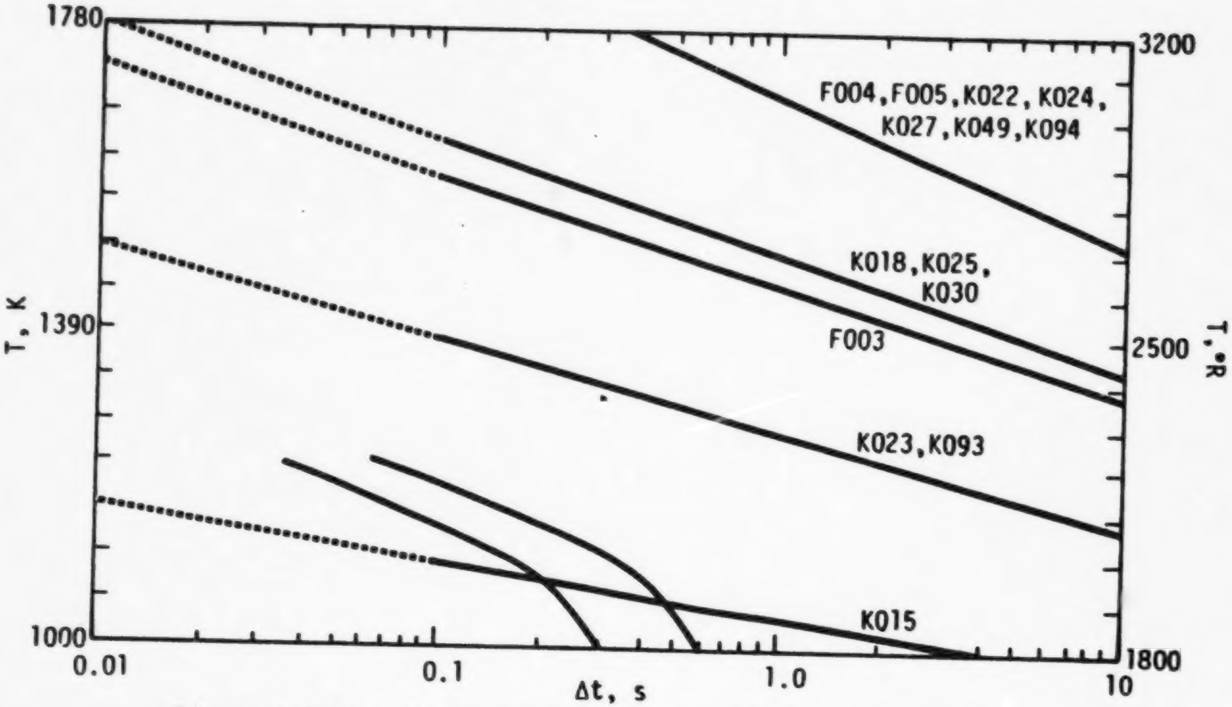

Figure 4.10-4. Hazardous waste destructibility predictions for multiple-hearth sewage sludge incinerators.

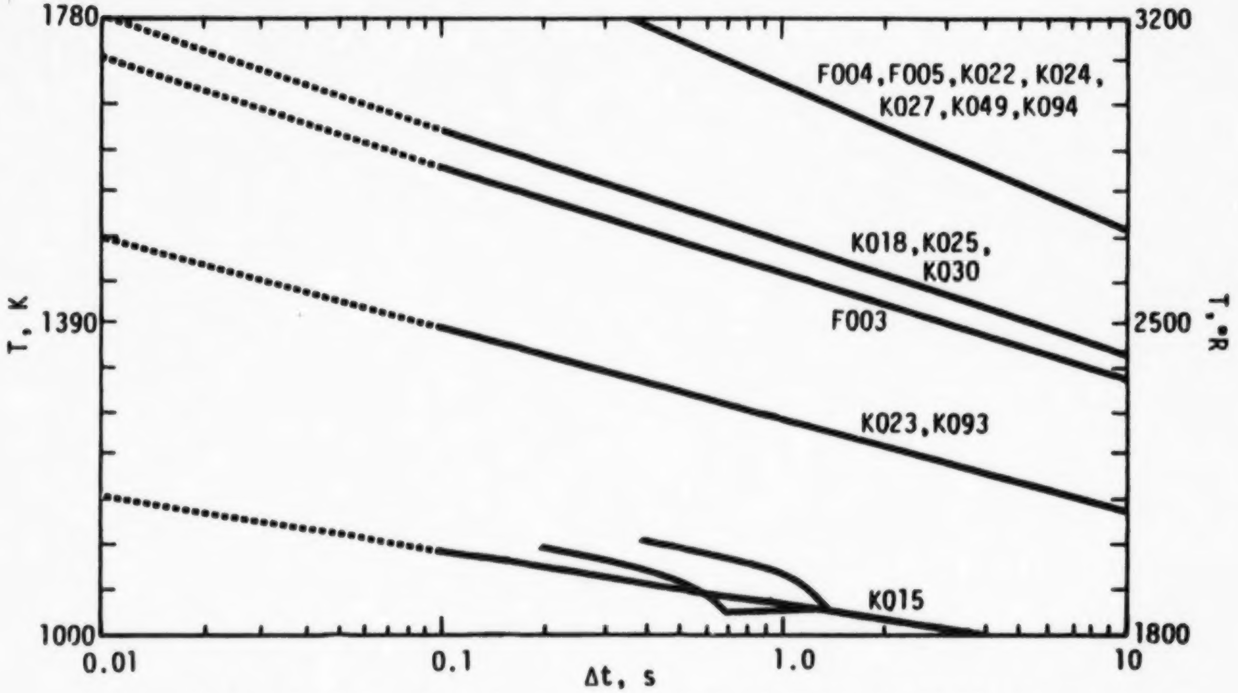

Figure 4.10-5. Hazardous waste destructibility predictions for fluid-bed sewage sludge incinerators.

TABLE 4.10-1. APPLICABILITY OF MULTIPLE-HEARTH SEWAGE SLUDGE INCINERATORS FOR THERMAL DESTRUCTION OF HAZARDOUS WASTES

K015	K023 K093	F003	K018, K025 K030	F004, F005, K022, K024 K027, K049, K094
Yes	No	No	No	No

TABLE 4.10-2. APPLICABILITY OF FLUID-BED SEWAGE SLUDGE INCINERATORS FOR THERMAL DESTRUCTION OF HAZARDOUS WASTES

K015	K023 K093	F003	K018, K025 K030	F004, F005, K022, K024 K027, K049, K094
Yes	No	No	No	No

feed. Most of the wear on process hardware is due to acid gases (HCl, H_2SO_4) and the scouring action of particulate that is already present in sewage sludge. The addition of hazardous waste in small proportions to the sludge would probably not accelerate this normal operating deterioration.

Acceptable amounts of hazardous waste feed--The net fuel value of sludge depends on the fuel value of its total combustible solids and the amount of water present. Sewage sludge generally has a high water content and, in some cases, fairly high levels of inert materials. As a result, its net fuel value is often low. Autogenous combustion of sludge is generally only possible when the solids content of the sludge is 30 to 35 percent or greater.[80] Because this is often difficult to achieve by conventional dewatering techniques, supplemental fuel is required for the combustion operation. If sludge is combined with other combustible materials in a co-combustion scheme, a furnace feed can be created that has both a low water concentration and a high enough heat value to sustain autogenous combustion, which could prove to be cost-effective.

The feed requirements will depend on the size and type of incinerator as well as the quality of the sludge. For example, a multiple-hearth incinerator processing 36 Mg/day (40 tons/day) (dry solid basis) will typically require 12×10^6 kJ/h (11×10^6 Btu/h) heat input. Based on a maximum hazardous waste input of 10 percent of the total heat input, the amount to be charged in this example should be no greater than 1×10^6 kJ/h (1×10^6 Btu/h), based on the heat content of the waste. This assumes that the waste is low in water content and inert solids.

Provisions for waste introduction--In the multiple-hearth incinerator the sludge is conveyed to the upper hearth of the incinerator, and mechanical rakes move the sludge from one hearth to the next lower hearth, where the sludge is sequentially dried and burned and the ashes cooled.[82] In the fluid-bed incinerator the sludge is injected directly into the bed, usually with screw feeders or spray nozzles. Problems with the feed system occur more often in the fluid-bed incinerator than in the multiple-hearth incinerator; the feed system will jam if the sludge is overdried.

If the waste can be added directly to the sludge before it enters the incinerator, no additional waste handling provisions are required for introducing the hazardous waste. This is especially true in the case of other waste sludges. If the hazardous waste is in a liquid state, atomization may be necessary to insure rapid and uniform vaporization and efficient combustion. The deisgn of the required additional feed and atomization system will be based on each individual furnace and waste stream. Section 2 provides a detailed discussion on hazardous waste handling and firing.

4.10.2.2 Geographic Matching--

Sewage sludge incineration has been practiced since the early part of the century and is widely used in this country. As of 1977, there were approximately 340 multiple-hearth and 60 fluid-bed incinerators in the United States; fluid-bed incinerators are a newer design and are gaining in popularity. Also, the anticipated banning of ocean disposal of sewage sludge will necessitate the use of alternative disposal methods, and the use of incinerators may increase along coastline states. Inasmuch as the use of sewage sludge incineration is widespread, there should be no problem in matching hazardous waste generation sites with locations of potential incineration processes. Hazardous waste category K015 is generated in only two plants, however; therefore the applicability of sewage sludge incinerators for the destruction of wastes in this category would be limited to incinerators near these two plant sites. If further study should prove that sewage sludge incineration was feasible for other hazardous waste categories than those indicated on Tables 4.10-1 and 4.10-2, then the widespread distribution of these incinerators would be an advantage.

4.10.2.3 Environmental Factors--

Impact on air pollution control devices--Because of the violent upward movement of combustion gases with respect to the burning sludge, particulate emissions are a major emission problem in both multiple-hearth and fluid-bed incinerators. Although dry sludge may contain from 1 to 2 percent sulfur by weight, sulfur oxides are not emitted in significant amounts in sludge burning compared with those emitted in many other combustion processes. Similarly, because incineration temperatures are lower than 980°C (1800°F) in fluidized-bed incinerators, nitrogen oxides are not formed in great amounts.[13] Nitrogen oxides may be a concern, however, if incineration temperatures are raised to destroy hazardous wastes. Table 4.10-3 provides a list of emission factors for sewage sludge incinerators based on data compiled by the EPA.[13]

TABLE 4. 10-3. EMISSION FACTORS FOR SEWAGE SLUDGE INCINERATORS[a]

	Emissions[b]			
	Uncontrolled[c]		After scrubber	
Pollutant	lb/ton	kg/Mg	lb/ton	kg/Mg
Particulate	100	50	3	1.5
Sulfur dioxide	1	0.5	0.8	0.4
Carbon monoxide	Neg	Neg	Neg	Neg
Nitrogen oxide (as NO_2)	6	3	5	2.5
Hydrocarbon	1.5	0.75	1	0.5
Hydrogen chloride gas	1.5	0.75	0.3	0.15

[a] Reference 13.

[b] Unit weights in terms of dried sludge.

[c] Estimated from emission factors after scrubbers.

Whereas incineration may enable complete destruction of hazardous materials, the combustion products may not be environmentally acceptable if emitted to the atmosphere. Therefore, certain wastes should not be incinerated unless the combustion products are treated with a suitable emission control device. Wastes of concern include chlorinated hydrocarbons, materials containing heavy metals, and waste with high sulfur content.[82]

Experimental data indicate that emissions of metals increase substantially as the combustion temperature increases.[83,84] If the temperatures of these incinerators are raised above normal operating levels to insure complete combustion of the organics in the hazardous waste, this can be a significant concern. These metal emissions also tend to be enriched on smaller submicron particulate, which makes them very difficult to control with conventional air pollution control equipment.

Because of the wide variability of sludge wastes that are currently incinerated, most facilities currently depend on versatile air pollution control equipment. High-efficiency wet scrubbers usually provide the necessary versatility, as chemical solutions can be suitably varied to treat different effluent contaminants. The required addition of control equipment to maintain air quality at higher temperatures may make the burning of hazardous wastes cost-prohibitive.

Environmental impact--Fugitive emissions can occur from improper handling and transport of the hazardous waste. A spill-prevention countermeasure and control plan must be developed, along with good housekeeping practices, to minimize discharges of the hazardous waste to the environment.

4.10.2.4 Institutional Factors--

Because of the nature of the sewage sludge incineration (i.e., treatment and disposal of a waste through combustion), there is no product to be adversely affected and thus no potential exposure to a consumer.

REFERENCES

1. U.S. Environmental Protection Agency. Resource Conservation and Recovery Act, Subtitle C; Background Document. Office of Solid Waste, Washington, D.C. November 14, 1980.

2. Mitre Corporation. Guidance Manual for Evaluating Permit Applications for the Operation of Hazardous Waste Incinerator Units. 1981.

3. Acurex Corporation. A Technical Overview of the Concept of Disposing of Hazardous Wastes in an Industrial Boiler. Prepared for U.S. Environmental Protection Agency, Cincinnati, Ohio. 1981.

4. Benson, S. W. The Foundations of Chemical Kinetics. McGraw-Hill. 1960. Chapters 10 and 11.

5. Weast, R. C. CRC Handbook of Chemistry and Physics. CRC Press, Inc., Boca Raton, Florida. 1980.

6. Domalski, E. S., W. H. Evans, and T. J. Jobe, Jr. Thermodynamic Data for Waste Incineration. Prepared for the American Society of Mechanical Engineers. NBSIR 78-1479. New York, New York. 1978.

7. Levenspiel, O. Chemical Reaction Engineering. Second Edition (1972). John Wiley and Sons, Inc., New York, N.Y.

8. Memorandum from L. R. Waterland and C. D. Wolbach, Acurex Corporation, Mountain View, California, to R. A. Olexsey, U.S. Environmental Protection Agency (IERL), Cincinnati, Ohio, September 21, 1981.

9. Industrial Gas Cleaning Institute. Air Pollution Control Technology and Costs in Nine Selected Areas. Stanford, Connecticut. Contract No. 68-02-0301. 1972.

10. Chews, F. H. Heavy Clay Technology. 2d Ed. Academic Press, London. 1969.

11. Kirk-Othmer. Encyclopedia of Chemical Technology. 3d Ed., Vol. 5. John Wiley & Sons, New York. 1979.

12. Personal communication from J. Blazina, Swindall Rust, to M. Taft, PEDCo Environmental. 1981.

13. U.S. Environmental Protection Agency. Compilation of Air Pollution Emission Factors. 3d Ed. Research Triangle Park, North Carolina. Publication No. AP-42, August 1977.

14. LeSourd, D. A., et al. Comprehensive Study of Air Pollution Sources to Assess the Economic Effects of Air Quality Standards. Vol. 1. U.S. Government Printing Office, Washington, D.C. December 1970.

15. Machine Design Waste Sludges Used To Make Better Insulating Bricks. 53(13), 1981.

16. Directory of Brick Manufacturers. Brick Institute of America, McLean, Virginia. 1974.

17. Product Directory of the Refractories Industry in the United States. Refractories Institute, Pittsburgh, Pennsylvania. 1972.

18. Directory, Vitrified Clay Sewer Pipe Industry. National Clay Pipe Institute, Crystal Lake, Illinois. 1972.

19. The Mitre Corp. Guidance Manual for Evaluating Permit Applications for the Operation of Hazardous Waste Incinerator Unit. EPA 68-01-6092, 1981.

20. Personal communication from G. Robinson, Clemson University, to M. Taft, PEDCo Environmental, Inc., June 1981.

21. Kirk-Othmer. Encyclopedia of Chemical Technology, 3d Ed., Vol. 4. John Wiley and Sons, New York, New York. 1978.

22. Mantell, C. L. Carbon and Graphite Handbook. John Wiley and Sons, New York, New York. 1968.

23. Gerstle, R. W., et al. Industrial Process Profiles for Environmental Use: Chapter 4. Carbon Black Industry. EPA-600/2-77-023d, February 1977.

24. PEDCo Environmental, Inc. Chemical Hazard Information Profile - Carbon Black. August 1, 1976.

25. Spinosa, E. D., et al. Summary Report on Emissions from the Glass Manufacturing Industry. EPA-600/2-79-101, April 1979.

26. Kirk-Othmer. Encyclopedia of Chemical Technology. 2d Ed., Vol. 10. John Wiley & Sons, Inc., New York, New York. 1966.

27. Stockham, J. D. The Composition of Glass Furnace Emissions. Presented at the 63rd Annual Meeting of the Air Pollution Control Association, St. Louis, Missouri, June 14-18, 1970.

28. Danielson, J. A. Air Pollution Engineering Manual. USPHS Publication No. 999-AP-40, 1967.

29. Franz, C. N., et al. Glass Furnace Particulate Emission Control Equipment. Presented at the 32nd Annual Conference on Glass Problems, University of Illinois, Urbana, Illinois, November 11, 1971.

30. Personal communication from Jerry Corbo, Johns-Manville, Parkersburg, W. Virginia, to Doug Orf, PEDCo Environmental, August 13, 1981.

31. Personal communication from Harry Grell, Libby-Owens-Ford Company, Toledo, Ohio, to Doug Orf, PEDCo Environmental, August 13, 1981.

32. Unpublished data received from Mr. R.L. Jacks of Teller Environmental Systems, Inc., New York, New York, November 7, 1972.

33. Personal communication from Hal Severin, Johns-Manville, Parkersburg, W. Virginia, to Doug Orf, PEDCo Environmental, August 13, 1981.

34. Personal communication from Ray Schick, Glass Packaging Institute, Washington, D.C., to Doug Orf, PEDCo Environmental, August 24, 1981.

35. Personal communication from Bob Laughman, Anchor Hocking Corporation, Lancaster, Ohio, to Doug Orf, PEDCo Environmental, August 14, 1981.

36. Department of Commerce. Annual Survey of Manufacturers. December 1980 (contains 1978 data).

37. Strassburger, J., et al. Blast Furnace - Theory and Practice. Vol. I. 1969.

38. Keenan, G. F., and D. M. Morrison. A Current Look at Pulverized Coal Injection for Blast Furnaces. Iron and Steel Engineer, October 1977.

39. 33 Metal Producing; World Steel Industry Data Handbook, Volume I, The United States. 1978.

40. Pietrucha, W. E., and R. L. Deily. Steel Industry in Brief: Data Book U.S.A. Institute for Iron and Steel Studies. 1979-80.

41. Sciulli, C. M., and D. G. White. Optimization of Fuel Injection into the Blast Furnace. In: Iron Making Proceedings, Volume 34, Toronto 1975. A Publication of the Iron and Steel Society of AIME. 1975.

42. Ashton, J. D., and J. E. R. Holditch. Homogenized Oil Injection at Dopasco. In: Iron Making Proceedings, Volume 34, Toronto, 1975. A publication of the Iron and Steel Society of AIME. 1975.

43. Personal communications from Robert C. McCrillis of Industrial Environmental Research Laboratories, Environmental Protection Agency, Research Triangle Park, North Carolina, September 16, 1981.

44. Mudd, S. W. Basic Open Hearth Steel Making. Physical Chemistry of Steel Making Committee, Iron & Steel Division, The Metallurgical Society of AIME. 1964.

45. AIME. Industrial Minerals and Rocks. 4th Ed. Port City Press, Baltimore, Maryland. 1975.

46. Berger, T. R. Lightweight Aggregate - Newest Concrete Material. Rock Products, 74(10), October 1971.

47. Expanded Shale Clay and Slate Institute. 1971. Lightweight Concrete - History, Applications and Economics. Washington, D.C.

48. Personal communication from L. Lawson, Solite, to M. Taft, PEDCo Environmental, Inc., September 1981.

49. Reedy, R. W. Lightweight Aggregates Part 1: Raw Materials. Pit and Quarry, 63(7), January 1971.

50. Reedy, R. W. Lightweight Aggregates Part 2: Plant Design. Pit and Quarry, 63(10), April 1971.

51. Personal Communication from Mr. J. Evans, Fuller Company, to Ms. M. Taft, PEDCo Environmental, Inc., October 1981.

52. Reedy, R. W. Lightweight Aggregates Part III: Selection of Equipment. Pit and Quarry, 64(2), August 1971.

53. Reedy, R. W. Lightweight Aggregates Part IV: Rotary Kiln Operation. Pit and Quarry, 64(5), November 1971.

54. Cohen, S. M., and N. W. Biege. Lightweight Aggregate Designing and Operating for Quality Product. Presented at the Annual Spring 1972 Meeting of the American Ceramic Society, Washington, D.C. 1972.

55. Personal communication from H. Robinson, Expanded Shale Clay and Slate Institute, to M. Taft, PEDCo Environmental, Inc., October 1981.

56. U.S. Environmental Protection Agency. Standards Support and Environmental Impact Statement. Vol. 1: Proposed Standards of Performance for Lime Manufacturing Plants. EPA-450/2-77-007a. 1977.

57. U.S. Department of the Interior. Mineral Industry Surveys, Lime in 1980. Bureau of Mines, Washington, D.C. 1980.

58. Kirk-Othmer. Encyclopedia of Chemical Technology. Vol. 14, 3d Ed. John Wiley and Sons, New York. 1978.

59. Kearney Management Consultants. Feasibility of Using Lime Kilns to Burn Hazardous Wastes. Prepared for the U.S. Environmental Protection Agency under Contract EPA 68-03-256. Alexandria, Virginia. 1981.

60. Personal Communication from Mr. F. Schwarzkopf, Kennedy Van Saun Corp., to Ms. M. Taft, PEDCo Environmental, Inc., 1981.

61. U.S. Department of the Interior. Lime, A chapter from Mineral Facts and Problems. Preprint from Bulletin 671 of the Bureau of Mines. 1980.

62. Robertson, J. L. Kiln Length, Diameter, and Speed Promote Formation of Ash Rings. Rock Products, 83(12), December 1980.

63. Personal Communication from Mr. E. Cohen, U.S. Environmental Protection Agency, Region III, to Ms. M. Taft, PEDCo Environmental, Inc., September 1981.

64. Personal Communication from Mr. Gutschich, National Lime Association, to Ms. Taft, PEDCo Environmental, Inc., July 1981.

65. U.S. Department of the Interior. Minerals Yearbook. Vol. I, Metals and Minerals. Bureau of Mines, Washington, D.C. 1978-79.

66. Hazelwood, D. L., F. J. Smith, and E. M. Gartner. Assessment of Waste Fuel Use in Cement Kilns. EPA 68-03-2586, 1981.

67. Bonner, T., et al. Draft Engineering Handbook for Hazardous Waste Incineration. EPA 68-03-2550, 1980.

68. Biswas, A. K., and W. G. Davenport. Extractive Metallurgy of Copper. 2d Ed. 1980.

69. PEDCo Environmental, Inc. Industrial Process Profiles for Environmental Use: Chapter 29, Primary Copper Industry. EPA-600/2-80-170, July 1980.

70. U.S. Environmental Protection Agency. Background Information for New Source Performance Standards: Primary Copper, Zinc and Lead Smelters. Volume I, Proposed Standards. EPA-450/2-74-002a, October 1974.

71. PEDCo Environmental, Inc. Industrial Process Profiles for Environmental Use. Chapter 27, Primary Lead Industry. EPA-600/2-80-168, July 1980.

72. Gibson, F. W. The Buick Smelter of Amax-Homestake Lead Tollers. Chapter 25, AIME World Symposium on Mining and Metallurgy of Lead and Zinc, Vol. II, The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, New York. 1970.

73. Beilstein, D. H. The Herculaneum Lead Smelter of St. Joe Minerals Corporation. Chapter 24, AIME World Symposium on Mining and Metallurgy of Lead and Zinc, Vol. II. The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, New York. 1970.

74. Cross, F. L. Baghouse Filtration of Air Pollutants. Pollution Engineering, February 1974.

75. Paul, R. B. The Glover Lead Smelter and Refinery of the American Smelting and Refining Company, Glover, Missouri. Chapter 26, AIME World Symposium on Mining and Metallurgy of Lead and Zinc, Vol. II. The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, New York. 1970.

76. PEDCo Environmental, Inc. Industrial Process Profiles for Environmental Use: Chapter 18, Primary Zinc Industry. EPA-600/2-80-169, July 1980.

77. Stankovic, G. Fluo-Solids Roaster and Acid Plant at Trepca Lead and Zinc Mines and Refineries, Mitrovica, Yugoslavia. Chapter 4, AIME World Symposium on Mining and Metallurgy of Lead and Zinc, Vol. II. The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, New York. 1970.

78. Baker, D., et al. Suspension Zinc Concentrate Roaster and Acid Plant of the Bunker Hill Company, Kellogg, Idaho. Chapter 3, AIME World Symposium on Mining and Metallurgy of

Lead and Zinc, Vol. II. The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, New York. 1970.

79. Lund, R. E., et al. Josephtown Electrothermic Zinc Smelter of St. Joe Minerals Corporation, Monaca, Pennsylvania. Chapter 20, AIME World Symposium on Mining and Metallurgy of Lead and Zinc, Vol. II. The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, New York. 1970.

80. U.S. Environmental Protection Agency. Process Design Manual for Sludge Treatment and Disposal. EPA 625/1-79-011. September 1979.

81. Conway, R. A., and R. D. Ross. Handbook of Industrial Waste Disposal. 1980.

82. Sittig, M. Incineration of Industrial Hazardous Wastes and Sludges. 1979.

83. Trichon, R. T., et al. The Fate of Trace Metals in a Fluidized Bed Sewage Sludge Incinerator. Presented at the 1981 APCA Conference.

84. Takeda, N. and M. Hiraoka. Combined Process of Pyrolysis and Combustion for Sludge Disposal. Environmental Science and Technology, 10:(12), November 1976.

APPENDIX A

BACKGROUND DATA ON HAZARDOUS WASTES HAVING A POTENTIAL FOR THERMAL DESTRUCTION

APPENDIX A. HAZARDOUS WASTES WITH POTENTIAL FOR THERMAL DESTRUCTION[a]

Hazardous waste No.	Description of hazardous waste	Physical state	Components	Present disposal practice	Geographic distribution (% of total generation)	Annual generation, metric tons
F001	Spent halogenated solvents used in degreasing and sludges from the recovery of these solvents in degreasing operations	Organic liquid Sludges	Tetrachloroethylene Trichloroethylene Methylene chloride 1,1,1 trichloroethane Carbon tetrachloride Chlorinated fluorocarbons			99,000
F002	Spent halogenated solvents and still bottoms from the recovery of these solvents	Organic liquid Still bottoms	Tetrachloroethylene Methylene chloride Trichloroethylene 1,1,1 trichloroethane Chlorobenzene 1,1,2 trichloro-1,2,2 trifluorethane o-dichlorobenzene Trichlorofluoromethane			
F003	Spent nonhalogenated solvents and the still bottoms from the recovery of these solvents	Organic liquid Still bottoms	Xylene Acetone Ethyl acetate Ethyl benzene Ethyl ether Methyl isobutyl ketone n-butyl alcohol Cyclohexanone Methanol			
F004	Spent nonhalogenated solvents and still bottoms from recovery of these solvents	Organic liquid Still bottoms	Cresols Cresylic acid Nitrobenzene			
F005	Spent nonhalogenated solvents and the still bottoms from recovery of these solvents	Organic liquid Still bottoms	Toluene Methyl ethyl ketone Carbon disulfide Isobutanol Pyridine			
K015	Still bottoms from distillation of benzyl chloride	Organic sludge	Acetonitrile Acrylamide Benzal chloride Residuals-alkali chlorides	Incineration, landfill	(2 plants)	5,300
K016	Heavy ends or distillation residues from production of carbon tetrachloride	Organic	Heavy chlorinated hydrocarbons Hexachlorobenzene Hexachlorobutadiene Carbon tetrachloride Hexachloroethane Perchloroethylene	Landfill, incineration	W. Virginia (20%) Texas (40%) California (5%) Louisiana (14%) Alabama (13%) Kentucky (4%) Kansas (4%)	3,200
K017	Heavy ends (still bottoms) from the purification column in the production of epichlorohydrin	Organic liquid	Trichloropropane (70%) Chloroethers (14%) Dichloropropanols (10%) Epichlorohydrin (2%) Chlorinated aliphatics (4%)	Holding ponds prior to incineration	Texas Louisiana	11,000

(continued)

APPENDIX A (continued)

Hazardous waste No.	Description of hazardous waste	Physical state	Components	Present disposal practice	Geographic distribution (% of total generation)	Annual generation, Mg
K018	Heavy ends from fractionation column in ethyl chloride production	Organic liquid	Heavy chlorinated organics (43%) Trichloroethylene (32%) 1,2 dichloroethane (22%) Ethyl chloride (3%)	Land disposal, incineration	Texas Louisiana New Jersey California	35,000
K019	Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production	Organic solid	Ethylene dichloride 1,1,1-trichloroethane 1,1,2-trichloroethane Tetrachloroethane Trichloroethylene Tetrachloroethylene Carbon tetrachloride Chloroform Vinyl chloride Vinylidene chloride Tars Residuals-metal chlorides (Fe, Al, Cu, Sb, Na)	Land disposal	Louisiana (49%) Texas (34%) Kentucky (7%) Puerto Rico (8%) California (2%)	6,346,000
K020	Heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production	Organic solid	Ethylene dichloride 1,1,1-trichloroethane 1,1,2-trichloroethane Tetrachloroethane Trichloroethylene Tetrachloroethylene Carbon tetrachloride Chloroform Vinyl chloride Vinylidene chloride Tars Residuals-metal chlorides (Fe, Al, Cu, Sb, Na)	Incineration, landfill	Louisiana (46%) Texas (33%) Kentucky (12%) Puerto Rico (7%) California (2%)	3,776,000
K022	Distillation bottom tars from the production of phenol/acetone from cumene	Organic sludge (solid)	Tars (>90%) Phenol Acetophenone Cumy phenol Residuals-$NaSO_4$	Landfill, incineration	Widespread	45,000-100,000
K023	Distillation light ends from the production of phthalic anhydride from naphthalene	Liquid	Phthalic anhydride (90.5%) Maleic anhydride (9.5%)	Incineration, offsite disposal	Pennsylvania (48%) Illinois (38%) New Jersey (14%)	952.6
K024	Distillation bottoms from the production of phthalic anhydride from naphthalene	Organic sludge	Phthalic anhydride (<50%) 1,4 naphthoquinone (<50%) Polynuclear tarlike materials	Landfill, incineration	Pennsylvania (48%) Illinois (8%) New Jersey (14%)	2,268

(continued)

APPENDIX A (continued)

Hazardous waste No.	Description of hazardous waste	Physical state	Components	Present disposal practice	Geographic distribution (% of total generation)	Annual generation, Mg
K025	Distillation bottoms from the production of nitrobenzene by the nitration of benzene	Organic sludge	Meta-dinitrobenzene (94%) 2,4-dinitrotoluene (6%) Nitrobenzene (trace)	Landfill	New Jersey (24.8%) W. Virginia (16.9%) Texas (25.1%) Mississippi (27.1%) Louisiana (6.1%)	166-205
K026	Stripping still tails from the production of methyl ethyl pyridines	Aqueous	Paraldehyde (75%) Pyridines Picolines Sulfuric acid Soluble acetates Phenol (very low conc.)	Water treatment lagoons, sludge to landfill	Indiana b	720 (1973)
K027^c	Centrifuge and distillation residues from toluene diisocyanate production	Organic sludge	Polymer and tarlike matter (90%) Ferric chloride (6%) Waste isocyanates (3%) Toluene diisocyanate Toluene Diomine	Landfilled, drums in landfill	W. Virginia Louisiana Texas Ohio	6,000
K029	Waste from the product steam stripper in the production of 1,1,1-trichloroethane	Aqueous liquid	1,2-dichloroethane (20%) 1,1,1-trichloroethane (80%) Vinyl chloride (trace) Vinylidene chloride (trace) Chloroform (trace)	Pits, landfilled	Texas (40.9%) Louisiana (59.1%)	2,350
K030	Column bottoms or heavy ends from the combined production of trichloroethylene and perchloroethylene	Organic liquid	Hexachlorobutadiene (33.8%) 1,1,2,2-tetrachloroethane (23%) Hexachlorobenzene (20%) 1,1,1,2-tetrachloroethane (6.3%) Ethylene dichloride (4%) Perchloroethylene (4.5%) beta-trichloroethane (4.5%) Pentachloroethane (3%)	Incineration, landfilled	Texas (41.8%) Louisiana (45.0%) Kentucky (6.1%) Kansas (4.4%) California (3.4%)	15,000
K032	Wastewater treatment sludge from the production of chlordane	Sludge	Hexachlorocyclopentadiene (other chlorinated cyclic organics)	Landfill	Illinois	
K033	Wastewater and scrub water from the chlorination of cyclopentadiene in the production of chlordane	Aqueous liquid	Hexachlorocyclopentadiene (other chlorinated cyclic organics)	Holding pond, filtered deep-well injection	Illinois	
K034	Filter solids from filtration of hexachlorocyclopentadiene in production of chlordane	Solids	Hexachlorocyclopentadiene (other chlorinated cyclic organics)	Landfill	Illinois	

(continued)

APPENDIX A (continued)

Hazardous waste No.	Description of hazardous waste	Physical state	Components	Present disposal practice	Geographic distribution (% of total generation)	Annual generation, Mg
K036	Still bottoms from toluene reclamation distillation in production of disulfoton	Aqueous liquid	Toluene, phosphorothioic acid esters, and other organics Residues-Na	Landfill	Missouri	120
K037	Wastewater treatment sludges from the production of disulfoton	Sludge (aqueous)	Toluene, phosphorodithioate, phosphorothioic acid esters Residues-Na	Landfill	Missouri	50
K039	Filter cake from the filtration of diethylphosphorodithioic acid in the production of phorate	Solid	Phosphorodithioic and phosphorothioic acid esters	Lagoons, holding ponds, land treatment, incineration	Missouri	
K040	Wastewater treatment sludge from the production of phorate	Sludge (aqueous)	Phorate, formaldehyde, phosphorodithioic and phosphorothioic acid esters	Lagoons, holding ponds, land treatment, incineration	Missouri	
K042	Heavy ends or distillation residues from the distillation of tetrachlorobenzene in production of 2,4,5-T	Organic sludge	Several chlorinated benzenes (hexachlorobenzene, dichlorobenzene)	Landfill	Kansas Michigan Arkansas (others not determined)	
K043	2,6-dichlorophenol waste from the production of 2,4-D	Organic liquid	2,6-dichlorophenol 2,4-dichlorophenol 2,4,6-trichlorophenol Residuals-Na Catalyst	Landfills	Arkansas	
K051	API separator sludge from the petroleum refining industry	Sludge	H_2O (53%) Oil (23%) Solids (24%) (sand, silt) Residuals-chromium, lead	Land disposal		400-800
K048	Dissolved air flotation (DAF) float from the petroleum refining industry	Sludge	H_2O (82%) Oil (12.5%) Solids (5.5%) (sand, silt) Residuals-chromium, lead	Land treatment and incineration Lagoon Landfill		4,000-29,000
K049	Slop oil emulsion solids from the petroleum refining industry	Sludge	H_2O (40%) Oil (43%) Solids (12%) (sand, silt) Residuals-chromium, lead	Land treatment and incineration Lagoon Landfill		2,000-10,000
K050	Heat exchanger bundle cleaning sludge from the petroleum refining industry	Sludge	H_2O (53%) Oil (11%) Solids (36%) (sand, silt) Residuals-chromium	Land treatment and incineration Lagoon Landfill		

(continued)

APPENDIX A (continued)

Hazardous waste No.	Description of hazardous waste	Physical state	Components	Present disposal practice	Geographic distribution (% of total generation)	Annual generation, Mg
K093[d]	Distillation light ends from the production of phthalic anhydride from ortho-xylene	Organic liquid	Phthalic anhydride (<100%) Maleic anhydride (trace)	Incineration	California (9.2%) Texas (16%) New Jersey (16%) Illinois (35%) Puerto Rico (9.3%)	2,223
K094[d]	Distillation bottoms from the production of phthalic anhydride from ortho-xylene	Organic sludge	Phthalic anhydride (<100%)	Incineration	California (9.2%) Texas (16%) New Jersey (16%) Illinois (35%) Puerto Rico (9.3%)	408
K095	Distillation bottoms from the production of 1,1,1-trichloroethane	Organic liquid	1,1,2-trichloroethane (39.7%) 1,1,1,2-tetrachloroethane (27.3%) 1,1,2,2-tetrachloroethane (31.6%) Pentachloroethane (1.4%)		Louisiana (100%)	64,420
K096	Heavy ends from the heavy ends column from the production of 1,1,1-trichloroethane	Organic liquid	1,2-dichloroethane (16.9%) 1,1,1-trichloroethane (27.3%) 1,1,2-trichloroethane (27.3%) Tetrachloroethanes and hexachloroethanes (28.3%) 1,1-dichloroethane (trace)		Louisiana (100%)	5,350
K097	Vacuum stripper discharge from the chlordane chlorinator in the production of chlordane	Organic liquid	Chlordane Heptachlor Other chlorinated wastes	Holding pond	Illinois (100%)	Not known

[a] Sources: Mite Corporation. Guidance Manual for Evaluating Permit Applications for the Operation of Hazardous Waste Incinerator Units. 1981; U.S. Environmental Protection Agency. Background Document Resource Conservation and Recovery Act. Subtitle C - Identification and Listing of Hazardous Waste. Office of Solid Waste. November 14, 1980.

[b] 1980 Directory of Chemical Producers.

[c] The constituents of this waste react violently with water.

[d] Incomplete combustion can form various phthalate esters.

APPENDIX B

INITIAL LISTING OF HIGH-TEMPERATURE PROCESSES

APPENDIX B. INITIAL LISTING OF HIGH-TEMPERATURE PROCESSES

Industry	Product	Process	Furnace type	Number of units	Process temperature	
					°C	°F
Organic chemicals	Acetylene	Combustion	BASF converter	3 plants	649	1200
	Biphenyl		Tublar coil reactor		600-800	1112-1472
	Carbon tetrachloride	Chlorinalysis	Reactor	11 plants	650	1202
	Carbon disulfide		Fixed bed catalytic reactor	5 plants	550-651	1022-1202
	Benzene	Hydrodealkylation	Fixed bed catalytic reactor	32 plants (4830 Mg/y)	538-649	1000-1200
	Isoprene		Catalytic reactor		600	1112
	Methacrylonitrile		Fixed bed catalytic reactor		800-900	1472-1652
	Methylcyclohexanone		Fixed bed multitublar reactor		630	1166
	Formaldehyde		Converter		816	1500
Carbon black	Carbon black	Cracking (furnace process)	Steel reactor	30 plants	760	1400
	Carbon black	Thermal cracking (thermal process)	Refractory-lined cylindrical furnace	3 plants	1320-2100	2400-3800
Petrochemicals	Olefins (ethylene)	Thermal cracking	Tubular	35 plants	816-871	1500-1600
	Synthesis gas	Catalytic steam hydro. reforming	Steam reforming		651-1050 or 1400-1800	1202-1922 or 2552-3272
Explosives	Nitric acid	Ammonia oxidation process	Catalytic oxidizer	5 plants	800-960	1472-1760
Lime	Lime	Calcination	Rotary kiln	485 kilns (90% are rotary) (21 million tons/yr)	1090-1320	2000-2400
	Lime	Calcination	Vertical kiln		1200-1300 970-980	2192-2372 1780-1796
Clay	Bricks	Firing	Tunnel kiln or batch kiln	500 plants	900-1430	1652-2606
Phosphate rock and basic fertilizer materials	Slurried deflorinated phosphate rock	Calcination	Rotary kiln or fluid bed reactor		1400-1540	2552-2804
	Ammonia synthesis gas	Steam reforming	Tubular		550-816	1022-1499
	Nitric acid	HNO_3 formation	Catalyst bed reactor	85 plants	800-900	1472-1652
	Phosphoric acid	Electric arc process	Electric arc furnace		1320	2400
	Elemental phosphorous	Furnace charge preparation		9 plants		
		• Nodulizing	Kiln		1200-1500	2192-2732
		• Calcining	Rotary kiln		1100-1320	2012-2400
		Electric furnace process (electrothermal reduction)	Electric arc furnace		1200	2912
	Phosphorous pentoxide	Phosphorous combustion (oxidation)	Combustion chamber	4 plants	200-2000	392-3632
	Sodium polyphosphate (Na_2HPO_4)	Calcination	Rotary kiln		300-900	572-1652
	Vitreous phosphates	Fusion	Rectangular furnace		700-1000	1292-1832
Sulfur, sulfur oxides, and sulfuric acid	Spent acid combustion	Combustion	Combustion furnace	167 plants (total sulfuric acid plants)	1000-1100	1832-2012
	Sulfuric acid		Air blown concentrator		677	1250

(continued)

APPENDIX B (continued)

Industry	Product	Process	Furnace type	Number of units	Process temperature	
					°C	°F
Iron and steel	Agglomerated product	Sintering	Sintering plant	71 agglomerating facilities	1300-1500	2372-2732
		Pelletizing	Kiln		1200-1370	2191-2499
	Coke production	Carbonization reduction)	Coke ovens	63 (44 Mg/yr)	1150	2102
	Pig iron	Reduction smelting	Blast furnace		1540	2800
		Smelting	Electric smelter		1480-1540	2700-2800
	Steel	Melting	Electric smelter	57 furnaces at 17 mills	1570-1640	2860-3000
		Retining (oxidation)	Open hearth (reverberatory)	86 furnaces (60 Mg/yr) 33 shops	1590-1640	2900-3000
		Rolling and shaping	Soaking pit furnace		1180-1340	2155-2440
	Iron	Melting	Cupola		1480-1540	2700-2800
	Steel	Melting	Acid open hearth	8	1640	3000
		Refining	Basic oxygen converter		1640-1820	3000-3300
		Refining	Rotary oxygen converter		1640-1820	3000-3300
			Electric induction		1090-1640	2000-3000
Nonferrous metal	Titanium tetrachloride	Chlorinated	Fluidized-bed furnace	12 plants	799-899	1470-1830
		Reduction (Kroll process)	Steel pot reactor	12 plants	849-899	1560-1650
	Titanium alloy	Melting	Cylindrical copper crucible	12 plants	1800	3272
	Titanium dioxide	Oxidation	Reaction chamber	17 plants (1.2 10^6 tons/yr)	999	1830
		Calcination	Direct-fired rotary kiln	12 plants (1.2 10^6 tons/yr)	999	1830
	Alumina	Sintering	Sinter plant	8 plants	1100-1200	2012-2190
		Calcination	Rotary kiln	6,650 x 10^3 metric Mg/yr 1979	1100-1200	2012-2190
	Electrode baking	Baking	Sunken pits		1200	2190
	Aluminum	Electrolytic reduction	Aluminum pots		951-999	1742-1830
		Refining or casting	Gas-fired holding furnace		699	1290
	Aluminum hydroxide	Calcination	Rotary kiln	6 plants (total AlO_3 producers	982	1800
	Copper	Smelting	Reverberatory	11 smelters	1000-1300	1832-2372
					1480-1930	2700-3500
		Roasting	Multiple hearth roaster	4 roasters (125-650 mt/d)	200-760	392-1400
			Fluidization roaster	4 roasters (700-1500 mt/day)	649-760	1200-1400
		Smelting	Electric furnace	3 smelters	999-1300	1830-2370
			Flash smelting	1 smelter	1100	2010
		Converting	Peirce-Smith converting	15 smelters	1180-1200	2150-2190
			Hoboken converting	1 smelter	1200	2190
	Copper (blister)	Smelting	Noranda furnace	1 furnace	1200	>2190
		Electric furnace slag treatment	Electric furnace	1 furnace	1200-1300	2190-2370
		Arsenic recovery	Godfrey roaster		649-699	1200-1290
	(anode)	Fire refining	Fire refining furnace		1100	2010
		Dore furnace	Sm. reverberatory furnace		1400	2550
		Sulfation roasting	Fluidization roaster	1 roaster	374-599	705-1110

(continued)

APPENDIX B (continued)

Industry	Product	Process	Furnace type	Number of units	Process temperature	
					°C	°F
Nonferrous metal (continued)	Lead	Sintering	Sinter plant	6 plants	799	1470
		Smelting	Blast furnace	6 plants	215-1220	419-2230
		Metal recovery	Slag fuming furance	6 plants	999-1200	1830-2190
			Dress reverberatory furnace		999-1200	1830-2190
		Reverberatory softening	Reverberatory (1300 Mg)		<700	<1290
		Kettle softening (melting)	Kettle		700	1290
		Antimony recovery	Not named		799-899	1470-1650
		Retorting (zinc recovery)	Faber-du-Favr type furnace		1260-1320	2300-2400
		Cupelling	Cupel furnace (2,850-11,300 Kg/charge)		1150	2100
	Zinc	Ferroalloy production (ferro-mangnesa)	Waelz kilns (rotary kiln)	1 plant	1300	2370
		Multiple-hearth roasting	Multiple-hearth roaster (50-60 tons/day)	2 smelters	688 949-977	1270 avg. 1740-1790 max.
		Suspension roasting	Suspension roaster (90-320 Mq/day)	1 plant at least 5 roasters	981	1796
		Fluidized bed roaster	Fluidized bed roaster		999-1050	1830-1920
		Sintering	Dwight-Lloyd-type sinter machine (220-500 tons/day)		1040	1900
		Vertical retorting (reduction/violatilization)	Vertical silicon-carbide retorts		1300-1400	2372-2550
		Electric retorting (reduction/violatilization)	Resistance-type electric furnace (90 mt/day)		899-1400	1650-2550
		Oxidizing	Grate-type furnace		999-1950	1830-3540
			Rotary or Waelz kiln		1300	2370
			Electrothermic furnace		899-1400	1650-2550
		Cadmium purification and casting (melting)	Horizontal retort		788-910	1450-1670
	Magnesium	Smelting	Crucible or pot-type	4 plants	816	1500
		Calcination	Calciner		704-1650	1300-3000
	Magnesium chloride	Electrolysis	Dow electrolytic cell		710	1310
		Ferrosilicon	Not named		1170	2140
Carbon	Coke	Calcinating	Horizontal and vertical rotary calciner		1200-1400	2192-2550
		Baking	Pit furnace or ring furnace		799-999	1470-1830
	Graphite	Graphitization	Electric furnace	28 plants (total graphite)	3000	5430
	Activated carbon	Oxidation activation	Retort		802-982	1475-1800
Miscellaneous chemicals	Fused sodium chloride	Electrolysis	Electrolysis cell		804	1480
	Calcium carbide		Carbide furnace		2000-2200	3630-3990
	Sodium silicate	Melting	Regenerative tank furance	42 plants	1200-1430	2200-2600
	Mineral wool		Cupola		1650	3000

(continued)

APPENDIX B (continued)

Industry	Product	Process	Furnace type	Number of units	Process temperature	
					°C	°F
Agricultural	Alfalfa	Dehydrating	Dehydrator		982-1090	1800-2000
Cement	Cement	Calcining	Rotary kiln	158 plants w/342 kilns	682-1650	1260-3000
		Drying	Rotary kiln	Avg. plant 536,000 TPY	599	1110
Glass	Glass	Melting	Glass melter (50-300 T/f)	9 plants (14,060 metric T/day) (338 plants)	1370-1710 593-871 927	2500-3100 1100-1600 1700
	Ceramic Coatings	Smelting	Rotary Hearth Crucible			
Sewage sludge incinerator	Multiple hearth			19 (wastewater treatment 1977)	316-649	600-1200
	Fluid bed			2 (wastewater treatment 1977)	649-816	1200-1500
Municipal solid waste combustors	None (steam)	Incineration	Water wall		760-1320	1400-2400
Industrial sludge combustors	None	Incineration	Liquid waste combustors		649-1650	1200-3000
		Incineration	Fluidized bed incinerator		760-871	1400-1600
		Incineration	Multiple hearth incinerator	125 installations (17,000 T/day)	760-982	1400-1800
		Incineration	Rotary kiln incinerator		871-1650	1600-3000